— SECTION B —

CHEMICAL SCIENCES

Contents

α-CYANO-β-PHENYLGLYCERIC ACID[1]

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Abstract

α-Cyano-β-phenylglyceric acid has been prepared by the action of aqueous sodium hypochlorite on α-cyano-β-phenylacrylic acid. It is somewhat unstable and decomposes slowly on standing.

When heated alone, it yields phenylacetic acid. Mild hydrolysis with mineral acid also gives phenylacetic acid. Hydrolysis under special conditions gives phenylpyruvic acid. The mechanism of these changes is discussed.

Theoretical

The reaction of hypochlorous acid or a hypochlorite with substances containing an ethylenic bond usually results in the formation of a chlorohydrin. Unsaturated acids such as acrylic, crotonic, maleic, and cinnamic are readily converted to chlorohydrins.

It was observed by McRae and Hopkins (2) that α-cyano-β-arylacrylic acids did not react with hypochlorite in a normal manner. Alkoxyarylacetic acids were formed when the starting material contained an alkoxyaryl group. α-Cyano-β-phenylacrylic acid itself gave chiefly oils and resinous substances.

It has been found in the present work that α-cyano-β-phenylacrylic acid reacts with sodium hypochlorite solution to give a rather unstable product. By shortening the time of the reaction and avoiding a rise in temperature, it was possible to isolate the substance, α-cyano-β-phenylglyceric acid (I). It has not been described previously.

$$C_6H_5CH{=}C(CN)COOH \xrightarrow{\text{NaOCl}} C_6H_5CH{-}C(CN)COOH \qquad (I)$$
$$\underset{\text{OH}\quad\text{OH}}{}$$
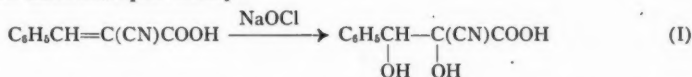
It is apparent that the chlorohydrin, if formed at all, is rapidly converted to the glyceric acid, since no chlorohydrin was isolated in any of our experiments.

α-Cyano-β-phenylglyceric acid exhibits a tendency to decompose on standing and breaks down rapidly when heated in the dry state at 100° C., giving phenylacetic acid. The latter reaction can be shown as resulting from the loss of carbon dioxide and hydrogen cyanide:
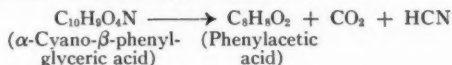
$$C_{10}H_9O_4N \longrightarrow C_8H_8O_2 + CO_2 + HCN$$

(α-Cyano-β-phenyl- (Phenylacetic
glyceric acid)   acid)

Positive identification of these two gases was made. Water is also produced, indicating that a different mode of decomposition occurs simultaneously. It is judged from inspection of the formula (I) that loss of water would not be compatible with formation of phenylacetic acid.

A quantitative study of the reaction showed that hydrogen cyanide is produced in about one-third the yield calculated from the equation above. Accordingly, it is concluded that, under the conditions of the experiment, about one-third of the material decomposes in the manner indicated and the remainder breaks down in some other fashion with loss of water.

Hydrolysis

The substance hydrolyses readily under the action of hydrobromic acid. The product is a mixture of phenylacetic and phenylpyruvic acids. By careful regulation of the conditions, the reaction may be controlled to give a good yield of either phenylacetic acid or phenylpyruvic acid as desired.

Using ice-cold 60% hydrobromic acid, the product is mainly phenylacetic acid. The mechanism underlying this change is not immediately apparent. It is possible that the glyceric acid (I) undergoes a pinacolone rearrangement involving migration of the CN, COOH or C_6H_5 group. Migration of the carboxyl group would result as follows:

$$C_6H_5CH \cdot C(CN)COOH \xrightarrow{HBr} \left\{ C_6H_5CH \text{---} C(CN)OH \right\} \longrightarrow C_6H_5CH_2$$
$$\quad\;\; | \quad\quad\; | \quad\;\;\text{(I)} \quad\quad\quad\quad\quad | \quad\quad\quad | \quad\quad\quad\quad\quad\quad\quad |$$
$$\quad OH \quad OH \quad\quad\quad\quad\quad\quad\quad\quad COOH \quad OH \quad\quad\quad\quad\quad\quad COOH$$
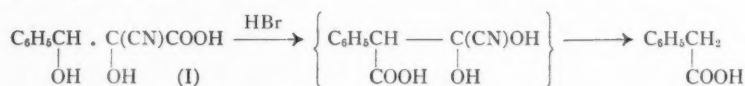
When α-cyano-β-phenylglyceric acid was treated with 52% hydrobromic acid at 25 to 30° C., phenylpyruvic acid was the main product. The yield was good. This procedure constitutes a new method of preparing phenylpyruvic acid. It may be found more convenient than previous methods, which have been described as tedious (1). The reaction is presumably as follows:

$$C_6H_5CH \cdot C(CN)COOH \xrightarrow{H_2O} C_6H_5CH \cdot CH \cdot COOH \longrightarrow C_6H_5CH \cdot CHCOOH$$
$$\quad\;\; | \quad\quad\; | \quad\;\;\text{(I)} \quad\quad\quad\quad\quad | \quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\diagdown\,O\,\diagup$$
$$\quad OH \quad OH \quad\quad\quad\quad\quad\quad\quad OH \quad OH \quad\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad C_6H_5CH_2COCOOH$$
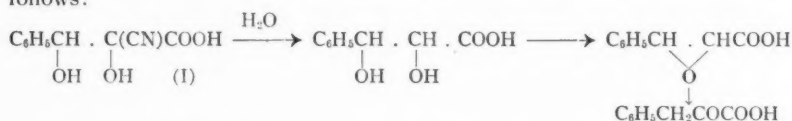
The action of ordinary 48% hydrobromic acid is less satisfactory. The hydrolysis requires several days at room temperature and results in a poor yield of phenylacetic acid.

It was at first thought that phenylpyruvic acid was an intermediate product in the hydrolysis and that phenylacetic acid is the normal end-product. However, upon treating a sample of phenylpyruvic acid with fuming hydrobromic acid, there was no reaction.

It is concluded that acid hydrolysis of α-cyano-β-phenylglyceric acid can occur in two ways. If a pinacolone rearrangement takes place first, the product is phenylacetic acid. If the hydrolysis of the CN group is the initial reaction, the product is phenylpyruvic acid.

Experimental

α-Cyano-β-phenylglyceric acid

α-Cyano-β-phenylacrylic acid (18 gm., 0.1 mole) was dissolved in 450 cc. of water and 75 cc. of 4% sodium hydroxide. The solution was cooled to 20° C. and mixed with 150 cc. of a molar solution of sodium hypochlorite (0.15 mole) also at 20° C.* The mixture was kept at 20° C. for one and one-half hours with occasional stirring, and was finally acidified with dilute hydrochloric acid (1 : 1). The precipitate, which formed gradually, was filtered off after one hour. The yield was 13 gm. When recrystallized from water, it formed glistening flakes, m.p. 88 to 89°†. The substance did not contain chlorine. Found: N, 6.72; equiv. 206. $C_{10}H_9O_4N$ requires: N, 6.76; equiv. 207. These figures taken in conjunction with the products of hydrolysis described below are believed to be sufficient to identify the substance as α-cyano-β-phenylglyceric acid. It is soluble in ethanol and ether, somewhat soluble in chloroform and benzene, and insoluble in hexane.

Upon standing for several weeks in a closed bottle at room temperature, the substance became sticky and finally changed to a thick brown liquid. The liquid had an unpleasant nitrile-like odour.

Hydrolysis to Phenylacetic Acid

A 250 cc. flask containing 10 gm. of α-cyano-β-phenylglyceric acid was surrounded by ice while 95 cc. of ice-cold hydrobromic acid (60% hydrogen bromide) was added slowly. Gas was evolved and a pale yellow precipitate formed. After remaining in the ice-bath for three to four hours, the mixture was diluted and the product was filtered off. It consisted of nearly pure phenylacetic acid (5.0 gm., 75% of theory). After one recrystallization from hexane, it melted at 75 to 76.5° and showed no depression in melting point when mixed with an authentic sample.

Hydrolysis to Phenylpyruvic Acid

Ten grams of α-cyano-β-phenylglyceric acid was mixed with 125 cc. of hydrobromic acid containing 52% of hydrogen bromide. The mixture was maintained at 25 to 30° C. for 24 hr. Phenylpyruvic acid was obtained as a white precipitate (5.0 gm.), m.p. 148 to 153° C. The yield was 60% of theory. After recrystallization from benzene the melting point was 158 to 159° C. The identity of the substance was confirmed by preparation of the acetyl derivative, which had the proper melting point of 172 to 174° C.

Resin was formed when the hydrolysis was carried out at temperatures above 30° C.

Pyrolysis

A weighed sample of α-cyano-β-phenylglyceric acid was placed in a U-tube and heated by a water bath at 90 to 100° C. Nitrogen was passed in and the exit gases were led through a series of absorption tubes. Water was absorbed

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* *A suspension of calcium hypochlorite is equally satisfactory.*
† *Melting points are corrected.*

by calcium sulphate, hydrogen cyanide by $N/2$ silver nitrate, and carbon dioxide by alkali. The hydrogen cyanide was determined by titration. The results are shown in Table I.

TABLE I

PYROLYSIS OF α-CYANO-β-PHENYLGLYCERIC ACID

Weight of sample	1.189 gm.	Water	0.076 gm. (74 mole %)
Weight of residue	0.871 gm.	Hydrogen cyanide	0.050 gm. (32 mole %)
		Carbon dioxide	0.166 gm. (65 mole %)
Loss	0.318 gm.	Total collected	0.292 gm.

A quantity of the acid was heated *in vacuo* in a short-path distillation apparatus, with the temperature of the heating bath at 90 to 100° C. The condensate amounted to about one-third of the weight of the sample. It was solid and was identified after recrystallization as phenylacetic acid.

References

1. HURD, C. D. and RATERINK, H. R.   J. Am. Chem. Soc. 56 : 1348-1350.   1934.
2. McRAE, J. A. and HOPKINS, C. Y.   Can. J. Research, 7 : 248-257.   1932.

THE EFFECT OF A FOREIGN SUBSTANCE ON THE TRANSITION: NH_4NO_3 IV $\rightleftharpoons$ NH_4NO_3 III[1]

Alan N. Campbell[2] and A. Jean R. Campbell[3]

Abstract

It is shown that the above transition can be repressed (metastably) by using in place of pure ammonium nitrate a solid solution of potassium nitrate in ammonium nitrate. With such a solid solution containing 8 to 10% potassium nitrate, the temperature of the transition III $\longrightarrow$ IV is depressed to about $-20°$ C. Such solid solutions can be prepared either by fusing the components together or by crystallizing from a mixed aqueous solution.

Introduction

This investigation was undertaken under the auspices of the Associate Committee on Explosives of the National Research Council of Canada. The original problem was to inhibit, over as large a temperature range as possible, the morphotropic change: NH_4NO_3 IV $\longrightarrow$ NH_4NO_3 III. It transpired, however, that this was impossible, but that the converse process of retaining form III in that state far below its normal transition temperature could readily be brought about. We show in this paper that the problem is solved by the use of a solid solution of potassium nitrate in ammonium nitrate. Although this result was obtained by us independently, we subsequently discovered that the same result had been arrived at about the same time by Prof. A. J. Allmand, working in England. Further questions arising out of the work were:— Is it possible to prepare solid solutions of potassium nitrate in ammonium nitrate by crystallizing from aqueous solution, instead of by fusing the components together, and, what is the lower limit of temperature to which the metastability of NH_4NO_3 III can be carried by the addition of potassium nitrate? Finally, is the metastability complete or does form III eventually revert to the stable form IV, in the presence of moisture?

From the point of view of the student of allotropy, ammonium nitrate is one of the most interesting substances. Under ordinary pressure it occurs in no fewer than five polymorphic modifications and, what is still more remarkable, all are stable in their appropriate ranges of temperature, in other words, the phenomena are all those of enantiotropy. Perhaps the best way to designate the forms is by the Roman numerals I to V. According to this classification, the form stable at room temperature is IV, the numbering decreasing towards higher temperature and increasing towards lower. The following table gives the crystallographic description and region of stability of each modification.

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[3] Wife of the senior author.

TABLE I

The modifications of ammonium nitrate

Modification	I	II	III	IV	V
Crystal system	Regular	Tetragonal	Rhombic	Rhombic tripyramidal	Tetragonal
Region of stability. °C.	169.6–125	125–83 (84)	83(84)–32	32–(−16) or −18	Below −16 or 18

The Literature

A very good summary is given in Gmelin's "Handbuch der anorganischen Chemie" (7).   In addition to this, the following original papers, which constitute the most up-to-date work on the subject, were consulted.   Cohen and van Lieshout (6) find the transition temperature III $\rightleftarrows$ IV as 32.3° C. and this seems to be the best value.   Cohen and Heldermann (4) deal with the preparation of the (physically) pure forms of III and IV.   Cohen and Kooy (5) had previously found for the densities of the modifications:

$$\text{IV} \quad d_{4°}^{32.3°} = 1.716$$
$$\text{III} \quad d_{4°}^{32.3°} = 1.654.$$

The heats of solution of the two forms, and, hence the heat of transition, are also obtained.   Müller (9) shows that potassium nitrate forms solid solutions with ammonium nitrate and that the transition temperature is thereby lowered.   The solid solutions used, however, were dilute.   A maximum of 0.78% potassium nitrate gave a depression of 1.820° C.   Jänecke, Eissner, and Brill (8), in their investigation of the system: NH_4NO_3–$(NH_4)_2SO_4$–H_2O, find that (a) the only double salt existing is $(NH_4)_2SO_4 . 2NH_4NO_3$, and (b) mixed crystals with ammonium nitrate are formed, whereby the transition temperature is depressed.   Wallerant (12), from a crystallographic study, deduces equilibrium diagrams for the binary systems comprising ammonium nitrate and one other alkaline nitrate.   The diagrams show a certain lack of knowledge of the phase rule, and from the results of this paper it would appear that he was occasionally dealing with metastable states, but the diagrams are of the greatest interest for the subject of this investigation.   In particular, the diagram for the system NH_4NO_3–KNO_3 led to some of the work detailed in this report.   According to Wallerant's diagram, the temperature of the transition III $\longrightarrow$ IV is depressed to subzero temperatures by the addition of about 5% potassium nitrate.   This is not true of the stable transition, since the process is not reversible, but it is true metastably.   Straub and Malotaux (11), in a short paper, supply the key to the solution of this problem. Using a specialized technique, they determined the transition point of ammonium nitrate containing 1% potassium nitrate in the form of solid solution, with rising and with falling temperature.   They found the transition temperature to be, with rising temperature 32.1° C., with falling temperature 23.8° C.   According to our work, one figure is too high and the other too low, but the results do show the important fact that form III remains metastable down

to a temperature much below its true transition temperature. Sieverts (10) finds that the velocity of transition is somewhat reduced in "ammonpulver", i.e., ammonium nitrate containing carbon.

We attacked the problem along two lines. First, by removing all nuclei of form III, we attempted to preserve form IV metastably above the normal transition temperature. This was found to be practically impossible. Second, we attempted, by forming solid solutions of ammonium nitrate with other substances, such as ammonium sulphate and potassium nitrate, to depress the transition point IV $\rightleftarrows$ III, either stably or metastably, to such an extent that form III became effectively stable at room temperature, and in this latter attempt we succeeded.

Experimental Work

EXPERIMENTS ON PURE AMMONIUM NITRATE

For the determination of transition points it was decided to employ two techniques, viz., the polarizing microscope and the dilatometer. Accordingly, a heated stage was constructed for a polarizing microscope but the instrument was hardly ever used. Unless the crystals are deposited from dilute solution on the microscope slide, they are not usually sufficiently transparent. On the other hand, the dilatometric method showed itself to be sensitive and easy to operate and this technique was therefore exclusively used. The dilatometers, of appropriate size, were constructed by ourselves of Pyrex glass. As inert liquid, toluene, distilled over phosphorus pentoxide, was used.

The experiments with pure ammonium nitrate were based on the well known work of Cohen (4), according to which every normally occurring crystalline form contains nuclei of the other forms which the substance may assume. It was thought that if it were possible to remove from form IV (stable at ordinary room temperature) all nuclei of III, it might be possible to retain IV metastably above its transition point (32.3° C.). It was recognized at the outset, however, that the long and complicated process whereby Cohen (4) obtains the (physically) pure forms was totally inapplicable to industrial work. Another possibility was that commercial ammonium nitrate, as used in explosives, might contain traces of impurity which catalyzed the change. The most obvious of such impurities was water, a well known catalyst for polymorphic changes, and ammonium nitrate is notoriously hygroscopic. However, anything of the nature of intensive drying was likewise out of the question from a commercial point of view.

Chemically pure ammonium nitrate (British Drug Houses, "certified chemical") was used in the earlier experiments. Later on, an 80-pound sack of ammonium nitrate was presented to us by the Consolidated Mining and Smelting Company of Canada, Trail, B.C., and this was used in the later work. The analysis accompanying the sack showed the material to be very pure.

As a first attempt, it was thought that if ammonium nitrate were prepared by crystallization at room temperature, instead of by boiling down, as in commercial practice, such a preparation might consist entirely of form IV, the form stable at room temperature.   Accordingly a solution of ammonium nitrate saturated at 20° C. was made up.   This was then warmed to 25° C. and filtered six times.   It was then placed in a closed container and dried, and filtered air sucked through it.   It was found, however, that the vapour pressure of a saturated solution of ammonium nitrate at 20° C. is so low that evaporation by the above process is inappreciable, even after several days. Accordingly, the above preparation was cooled in ice overnight and the resulting crop of crystals filtered in the morning.   This crop of crystals was kept at room temperature, first over water, then over sulphuric acid.   Two dilatometers were now prepared, one containing 45 gm. of pure, but untreated ammonium nitrate, the other 45 gm. of the above-mentioned ammonium nitrate, which had been left over water for 24 hr., and dried over sulphuric acid for 11 days.   Both dilatometers were now placed in a thermostat at 32.0° C. overnight.   In the morning, the toluene levels were read on a cathetometer.   The temperature was then raised 0.1° C. and kept at that for a further 24 hr.   The operations were then repeated.   Unfortunately, we were not at this time supplied with completely satisfactory apparatus, and during the fourth night of the experiment the temperature of the thermostat rose to 35.8° C.   On checking back to 32.3° C., it was found that the untreated ammonium nitrate had completely transformed, but the treated material only partially so.   A repeat of this experiment underwent the same fate, i.e., the temperature of the thermostat rose during the night to 39.5° C., as a result of which the treated specimen had completely transformed.   The untreated specimen transformed at 33.0° C.   In a third experiment a specimen of ammonium nitrate treated as described above but deliberately moistened with a few drops of water, transformed at 33.6° C.

A sample of ammonium nitrate, recrystallized as described above, was left over water for five days (as recommended by Cohen), then dried over sulphuric acid for 14 days.   Two specimens of this lot transformed at 34.0° and 33.0° C., respectively.

It will be seen from the above that our attempted purifications had not resulted in raising the transition temperature more than one or two degrees. In order to determine whether we were really dealing with the (physically) pure form IV, determinations of density were carried out.   The material used was recrystallized from water at 0° C., left over water for 24 hr., and dried over sulphuric acid for 11 days.   Three determinations of density were made with the following results.

$$1. \ d_{4°}^{32.2°} = 1.7162$$
$$2. \ d_{4°}^{32.3°} = 1.7150$$
$$3. \ d_{4°}^{32.0°} = 1.7197.$$

The untreated ammonium nitrate, dried over sulphuric acid for three days, had a density of $d_{4°}^{35.3°} = 1.6894$.

The above figures are to be compared with Cohen's figure of $d_4^{32.3°} = 1.716$.

A fourth specimen, crystallized as above, and dried over sulphuric acid for 25 days, had a density of $d_4^{32.5°} = 1.7204$. Hence, it appears that our method of preparing form IV is completely successful. Quantitative measurements of the expansion accompanying the transformation also indicated that the preparation was 100% form IV although it may be that, despite the treatment, nuclei of III are still present. Further experiments on pure ammonium nitrate were abandoned, since it appears that even with a form IV that is both chemically and physically pure (and dry), the transition point can be raised (metastably) only one or two degrees. It seems unlikely that the lattice of so soft a substance as ammonium nitrate can permanently resist thermal agitation above its transition point.

EXPERIMENTS WITH AMMONIUM SULPHATE AS ADDITION

These experiments were based on the work of Jänecke, Eissner, and Brill (8), according to which ammonium sulphate forms solid solutions with all forms of ammonium nitrate. Although the stable effect is to lower all transition points, it was thought possible that by rapid chilling, form I, in which the solid solubility is extensive, might be preserved metastably at room temperature. Accordingly, the following procedure was adopted:— A mixture of 3 gm. of ammonium sulphate and 97 gm. of ammonium nitrate was melted carefully with constant stirring; the mixture was completely liquid at 175° C. The molten mixture was then poured into a beaker surrounded by cracked ice, and left until the temperature had fallen below room temperature. This required 30 min. The mass was then ground and dried over sulphuric acid *in vacuo* for 24 hr. A dilatometric experiment was then carried out, the temperature being allowed to rise from room temperature. Transformation took place at 36° to 37° C. Further work with ammonium sulphate was abandoned at this point because of the papers by Wallerant (12) and by Straub and Malotaux (11). According to Wallerant, the temperature of the transition III $\longrightarrow$ II is raised and that of III $\longrightarrow$ IV enormously depressed, by the addition of a small quantity of potassium nitrate.

EXPERIMENTS WITH POTASSIUM NITRATE AS ADDITION

If the observations of Wallerant (12) are correct, the effect of the addition of, say, 5% potassium nitrate, is to render form III the only stable form between the ice and boiling points of water; the discontinuous volume change would thus be obviated. According, however, to Straub and Malotaux (11), the stable transition points are not affected to anything like the extent indicated by Wallerant, the observations of Wallerant referring to metastable transitions. It occurred to us, however, that if the metastability were sufficiently obstinate, by adding sufficient potassium nitrate to depress the transition III $\longrightarrow$ IV (metastably) below room temperature, the reverse transition IV $\longrightarrow$ III could not, of course, occur, and this we have found to be the case.

Thermal Analyses

The melts of potassium nitrate and ammonium nitrate were first subjected to thermal analysis, employing a sensitive technique, such as is used in metallographic work.   The following results were obtained.

Pure ammonium nitrate:

Freezing point	=	168.7° C.
Transition I $\longrightarrow$ II	=	125.8° C.
II $\longrightarrow$ III	=	Not detectable thermally (some evidence of delayed transition at 64° C.)

$$\text{III} \longrightarrow \text{IV} \quad = \quad 31.2° \text{ C.}$$

Pure ammonium nitrate: Substance powdered but not fused, temperature range = 100° to 30° C.

$$\text{II} \longrightarrow \text{III} \quad \text{T} = 81.65° \text{ C.}$$
$$\text{III} \longrightarrow \text{IV} \quad \text{T} = 31.58° \text{ C.}$$

1% potassium nitrate: Mixture fused, cooled, powdered, and examined between 100° and 18.5° C.

Possible slow change in the range 90° to 78° C.

$$\text{III} \longrightarrow \text{IV}. \quad \text{Change over range } 28.7° \text{ to } 22.9° \text{ C.}$$

Dilatometric Experiments

As the only transitions of importance to this work are III $\longrightarrow$ II and III $\longrightarrow$ IV, and these lie within the range of the dilatometer, we returned to this technique.   A fused mixture containing 1% potassium nitrate was kept in the ice-chest overnight (maximum temperature = 20° C.).   A portion (30 gm.) of this powdered substance was placed in a dilatometer, and the dilatometer filled with dry, ice-cold toluene.   The temperature was then allowed to rise from 13.4° C.   The transition temperature was found to lie in the range 30.1° to 31.2° C., i.e., a depression of transition temperature of only about 1.7° C. was observed in contradistinction to the very large depression indicated by Wallerant's graph.   This, however, is the stable (temperature rising) transition.

It seemed of interest to compare the volume increase accompanying the transformation IV $\longrightarrow$ III, in the presence of potassium nitrate, with that of pure ammonium nitrate.   Accordingly, the total displacement of the toluene column was observed, the radius of cross-section of the capillary measured ($r = 0.04905$ cm.), and the density of the mixture determined.   The expansion with pure ammonium nitrate is calculated from Cohen's figures as 3.77%. Our results are:

1% potassium nitrate: Expansion = 2.247%.
2% potassium nitrate: Expansion = 2.574%.

If Cohen's figures are correct, as presumably they are, the volume change is somewhat less, in the presence of potassium nitrate, when the transformation does occur.

The dilatometer experiments were now resumed. With 2% potassium nitrate, the stable (upwards) transition temperature was found to lie at 28.3° C.; the treatment was the same as in the previous case, viz., mixture kept in an ice-chest over night.

4% potassium nitrate: This preparation was treated differently, in that it was never cooled below room temperature (24.5° C.) until the beginning of the dilatometric experiment, when the dilatometer was placed in a bath at 15.9° C. *No transition was observed, up to 88.2° C.* This observation, at first disconcerting to us, receives its explanation from the work of Straub and Malotaux. The sample had never been cooled below the temperature necessary for the (metastable) transition III ⟶ IV. It was, therefore, throughout its history, form III. The temperature of stable transition is extrapolated from the previous results as about 24° C. Another sample of the 4% preparation was kept in a bath at 17° C. for 48 hr. This also showed no transition up to 28.3° C.

The density of the 4% preparation was obtained as
$$d_4^{32.2°} = 1.656.$$

3% potassium nitrate: Kept in bath at 17° C. for 24 hr. Slight indication of transition: $d_4^{32.3°} = 1.6536$.

The preceding experiments having shown that a great difference exists between the transition temperature on heating and that on cooling, a series of dilatometer experiments with falling temperature was now undertaken.

1% potassium nitrate: A new sample was prepared, cooled to room temperature, and ground. A portion (30 gm.) was placed in a dilatometer and the dilatometer kept overnight in a thermostat at 32.3° C. The temperature was then lowered progressively. After the transition with the falling temperature had been observed, the temperature was raised and the reverse transition observed. In solid solution, transition should, of course, take place over a range of temperature, not at a fixed temperature, but under ideal conditions of diffusion, etc., the range should be the same with ascending and descending temperature.

1% potassium nitrate	Temperature falling:	$T = 25.3°$ to $24.9°$ C.
	Temperature rising:	$T = 30.6°$ C.
2% potassium nitrate	Temperature falling:	$T = 20.2°$ C.
	Temperature rising:	$T = 28.3°$ C.
3% potassium nitrate	Temperature falling:	Transition begins at 18°; becomes rapid around 12° C.
	Temperature rising:	Transition begins at 26°; violent at 27.8° C.
4% potassium nitrate	Temperature falling:	Slight transition at 9.5° C.; increases greatly at 5.6° C.
	Temperature rising:	Transition begins at 23° C.; more marked at 25° C.

5% potassium nitrate Preparation kept overnight at 18° C.   Dilatometer heated from 23.45° to 32.2° C.; no transition. Dilatometer then cooled.

Temperature falling: Transition seemed to begin around 1° C.   Dilatometer kept in cracked ice overnight.

Temperature rising: Transition at 22° C.

Analysis of Specimens

The mixtures described as 1%, 2%, etc., potassium nitrate were made up synthetically.   Owing to volatilization and decomposition of the ammonium nitrate on melting, the compositions were not precisely those of the original weights.   The mixtures were therefore analysed by converting the potassium nitrate to potassium sulphate.   The method is not very sensitive and the error large, but the results are probably good enough for the work in hand. The results are:—

Nominal KNO_3 content, %	True KNO_3 content, %
1	0.986 ± 0.073
2	1.965 ± 0.084
3	3.163 ± 0.075
4	4.405 ± 0.115
5	5.126 ± 0.171

Densities of the Potassium Nitrate Solid Solutions

As the densities given above were determined without reference to the previous thermal history of the sample, they must be considered as more or less meaningless in the light of what has been said about the metastability of the transformation.   The present work was designed to take into account the previous thermal history, and to act as a check on the dilatometer results.

Two hundred grams of each of the mixtures was prepared by fusion and subsequent slow cooling.   This was ground, dried over sulphuric acid for 24 hr., sealed off in glass flasks, and kept in a thermostat at 32.3° C. for five days.   Each mixture should then have been in the stable III condition.   The density of each sample was then determined as follows:

KNO_3 content, %	$d_{4°}^{32.3°}$
0.989	1.620 : 1.616
1.965	1.647
3.163	1.651
4.405	1.664
5.126	1.671

If these figures are graphed, the density of 2% potassium nitrate is seen to be distinctly too high for a straight line relation. Since all the preparations are in the condition of form III and potassium nitrate is somewhat denser than ammonium nitrate, it is apparent that the formation of solid solutions in form III is attended by considerable expansion.

The temperature of the thermostat was then lowered to 22.55° C., at which temperature 1% potassium nitrate should have transformed to form IV but the others not.

The following figures were obtained:

KNO_3 content, %	$d_{4°}^{22.55°}$
0.980	1.6602
1.965	1.6313
3.163	1.6494
4.405	1.6611
5.126	1.6667

Somewhat surprisingly, the figures at the lower temperature are, with the exception of those for 1% potassium nitrate, slightly lower than those at 32.3° C. This may be error or it may be real, indicating some slow progressive change in the solid solution. The important thing, however, is the marked increase in density of the 1% potassium nitrate, indicating that this solid solution alone has passed the transition III $\longrightarrow$ IV. The increase in density, about 4 units in the second decimal place, is too large to be experimental error, but is still somewhat less than the change of density of pure ammonium nitrate (about 6 units in the second decimal place). This is in agreement with our direct observation of the volume change accompanying the transition, which we found to be distinctly less than with pure ammonium nitrate. Again, it is to be observed that the density of the transformed 1% potassium nitrate is also much less than that of pure ammonium nitrate in the same condition, indicating that potassium nitrate also forms solid solutions with form IV, and that these solid solutions are also formed with expansion.

As a check on the rapid work of the dilatometer, various solid solutions were kept in the thermostat at different temperatures for long periods, and the density determined. The transition would thus manifest itself as an abrupt change in density; at this time we still feared that the metastability might only be a question of time. The solid solutions were kept over concentrated sulphuric acid for 24 hr., then sealed off in glass flasks, and kept in the thermostat at 32.3° C. for five days. Samples were then removed for density determination and the flasks resealed. The temperature was then lowered to 22.55° C. (i.e., a temperature below the transition point of 1% potassium nitrate as determined by cooling in the dilatometer), kept at that for 24 hr., and the densities then determined. This procedure was then first repeated at 18.1° C. for 48 hr., and then finally in cracked ice overnight. The results are contained in Table II.

TABLE II

DENSITIES OF AMMONIUM NITRATE AT DIFFERENT TEMPERATURES

Temp., °C.	Potassium nitrate, %				
	1	2	3	4	5
	Density, $d_{4°}^{t°}$				
32.3	1.620	1.647	1.651		1.671
	1.616			1.664	
22.44	1.660	1.631	1.649	1.661	1.667
18.1	1.655	1.676	1.659	1.661	1.668
		1.678			
0.7		1.679	1.697	1.686	1.719

There are some discrepancies in the above figures, either due to experimental error (included air?) or to some slow secular change in the solid solution, but the qualitative result is the same as with the dilatometer, viz., the 1% potassium nitrate has undergone transformation at 22.5°, the 2% at 18.1°, the 3% partially at 18.1°, but completely at 0°, while the 4 and 5% had also changed completely at 0° C.

Analysis of Solid Solutions Prepared by Fusion

Six new preparations were made (1, 2, 3, 4, 5, and 6% potassium nitrate), ground, preserved over concentrated sulphuric acid, and analysed for potassium nitrate by conversion to potassium sulphate. The results were:

Nominal KNO₃ content, %	True KNO₃ content, %
1	0.9517 ± 0.0162
2	1.737 ± 0.008
3	2.780 ± 0.084
4	3.931 ± 0.06
5	4.741 ± 0.01
6	5.839 ± 0.014

Protracted Dilatometric Experiment

With the idea that the metastability might not really be permanent, we started the following experiment. New samples were prepared of 1 to 6% potassium nitrate and 10% potassium nitrate. These were dried over sulphuric acid for several days. Samples (30 gm.) of each were then placed in separate dilatometers, which were filled up with toluene that had been dried over phosphorus pentoxide. These dilatometers were then left in a thermostat at 32.3° C. overnight. They were thus all in the III condition at the start of the experiment. This experiment was begun September 26, 1941. After reading the toluene levels at 32.3° C. the thermostat temperature was lowered 1° to 31.3° C. and maintained at that value for 24 hr. On the following morning the toluene levels were again read, the temperature then lowered 1°, and so on.

On October 10, the 1% potassium nitrate transformed at 26.2° C. On October 21, the 2% potassium nitrate transformed at 21.3° C. By October 30 the temperature had been dropped to 16.3° C. and the temperature was kept at that value until January 9, because we had no means of obtaining a controlled temperature below 16.3° C. During this period, the 3% potassium nitrate underwent slow transformation. A cooling unit with thermostatic control was put into operation on January 9, and the temperature dropped 1° C. per day, as before. On February 10, the 4% potassium nitrate transformed together at 2.0° C. By February 28 the temperature had been lowered to −0.6° C., the 10% potassium nitrate (dry) and the 10% potassium nitrate (moist) remaining untransformed. On March 2, the "10% potassium nitrate moist" (1.7% H_2O) transformed at −0.1° C. after a week at this temperature. The "10% potassium nitrate dry" remained untransformed at −10.0° C. This confirms Allmand's statement that the stability is considerably reduced by the presence of moisture (vide infra).

Dilatometric Experiment with 10% Potassium Nitrate

In order to avoid the necessity of adding or abstracting toluene from a dilatometer with capillary bore, a dilatometer with relatively wide bore (about 2 mm.) was constructed and charged with 30 gm. of 10% potassium nitrate in solid solution. The sensitivity was much reduced by this procedure but it was calculated that total transformation (corresponding to a volume change of about 3%) would produce a displacement of several centimetres. With this apparatus it was possible to investigate between 95° and 0° C., without removal or addition of toluene. Starting from 20° C., the temperature was raised to 95° C., then lowered to 0° C., the whole operation occupying about three hours. No transition was observed.

EFFECT OF MOISTURE

According to Allmand (confidential report) if the moist sample is submitted to a cyclic treatment, that is, alternately heated to 55° C. and cooled to −20° C., an expansion (presumably representing partial transformation) occurs; the expansion is much less than corresponds to complete transformation. Our experiments had been carried out with well dried specimens, and even the toluene used was distilled from phosphorus pentoxide. Accordingly, two dilatometers were prepared, one filled with a sample of commercial ammonium nitrate which had been dried for six months over concentrated sulphuric acid, and which therefore approached to an intensively dried specimen, and the other with a sample of the same material to which 1 cc. of water had been added (charge, 30 gm.). The following were the results:—

Sample	Transition temperatures, °C.	
	Temp. rising	Temp. falling
Moist	34.9	28.9 : 30.2
Dry	34.9	29.2 : 30.4

It appears that in the case of pure ammonium nitrate, presence or absence of moisture has little effect, and this confirms our previous results.

It appears that Allmand's observations were carried out on compressed blocks and it is possible that the observed expansion is to be attributed to the interstices of the material. This effect would not be observed in the NH_4NO_3–KNO_3 mixed crystals in powdered form. Accordingly a 10% potassium nitrate (prepared by fusion) was introduced into a dilatometer having a wide bore and furnished with a reservoir at the top; the instrument was then sealed off at the top. Dilatometric readings were taken up to 95.0° C. and down to 0.1° C.; there was no evidence of a transition. Apparently the transition III ⟶ II is raised above 84° C., which is the value for pure ammonium nitrate.

To investigate the effect of moisture two dilatometers were filled, one with commercial ammonium nitrate which had been dried out for six months over concentrated sulphuric acid, the other with the same material which had been moistened. The following are the results:

	Transition begins	Trans. max. velocity
	Temperature falling	
Dry NH_4NO_3	29.7° C.	29.2° C.
Moist NH_4NO_3	29.4°	28.9°
	Temperature rising	
Dry NH_4NO_3	34.9°	34.9°
Moist NH_4NO_3	34.35°	34.9°
	Temperature falling	
Dry NH_4NO_3	30.85°	30.4°
Moist NH_4NO_3	30.85°	30.2°

The presence of moisture seems to have little effect on the hysteresis, although, of course, it is quite possible that the so-called "dry" sample still contained a trace of moisture.

Two dilatometers were now prepared with reservoirs at the top. These were charged with 10% potassium nitrate (prepared by fusion), one sample being "dry" the other being "moist". After addition of the indicator fluid (xylene) the dilatometers were sealed off. These were stabilized in a thermostat at 16° C. overnight. They were then heated to 50° C. and cooled to −20° C. (ice and salt) on alternate days; they were brought back to 25° C. each night, kept in the thermostat overnight, and the levels read the following morning. Three such complete cycles were carried out. The results were surprising. A *contraction* was observed, amounting to 0.38% for the dry specimen, and to 0.17% for the moist. Most of the contraction was observed in the first cycle. This was, however, probably a malobservation, for xylene

was observed to have condensed in droplets in the reservoirs. In the calculation of the above contractions, the density of 10% potassium nitrate was determined as $d_4^{25°} = 1.682$.

The preceding experiment was therefore repeated using sealed dilatometers without reservoirs, it having been found that the diameter of the dilatometer (about 1 mm.) was sufficient to take up the expansion. Care was taken to remove all trace of included air. Four complete cycles were carried out. The moist sample, in this case, showed a contraction of 0.4%, the dry sample no contraction at all. In view of the irregular nature and small amount of the effect we are inclined to attribute it to secondary causes, probably dissolved air. The probability is that 10% potassium nitrate *per se* shows no permanent volume change. Nevertheless, as shown above, a solid solution containing as much as 10% potassium nitrate will eventually transform below 0° C., if it is moist and if it is kept sufficiently long at that temperature (say −10° C.).

EFFECT OF SODIUM NITRATE IN THE PRESENCE OF POTASSIUM NITRATE

A ternary mixture of composition 72% ammonium nitrate, 20% sodium nitrate, and 8% potassium nitrate froze at the eutectic temperature of 117.5°C. We thought this might represent a convenient method of preparing the NH_4NO_3–KNO_3 solid solutions. A dilatometer was charged with this eutectic mixture and an experiment carried out. The dilatometer was allowed to cool from 130° C. Allotropic transformation, no doubt III $\longrightarrow$ IV, took place at 12° C. Apparently the presence of the sodium nitrate prevents the potassium nitrate from exerting its effect. The explanation is no doubt as follows. It is known that sodium nitrate and potassium nitrate form a continuous series of solid solutions above 130° C. (2). Below this temperature the solid solution breaks up into a conglomerate but the liberated potassium nitrate will not be entirely taken up by the ammonium nitrate, since the system is now largely solid. In other words, the content of potassium nitrate in the NH_4NO_3–KNO_3 solid solution is less than appears from the total potassium nitrate content, and hence the depressing effect on the transition temperature is not so great. The desired effect could no doubt be obtained by using a higher proportion of potassium nitrate.

Preparation of NH_4NO_3–KNO_3 Solid Solutions from Aqueous Solutions

The question as to the possibility of preparing solid solutions of potassium nitrate in ammonium nitrate, from the corresponding aqueous solutions, has already been answered in the affirmative, more or less, by the work of Caillart (3) and of Ando (1), who studied the system KNO_3–NH_4NO_3–H_2O at temperatures of 17° and 25° C. From the results of both it appears that mixed crystals of the ammonium nitrate type, containing up to about 30% potassium nitrate, can be obtained by crystallization from mixed solutions, and that the solid solution obtained is not greatly different in composition

from the equilibrium aqueous solution.   These results for room temperature do not necessarily apply to the temperatures of industrial crystallization, so the following experiments were carried out.   A mixture of the following composition:— 2720 gm. ammonium nitrate, 272 gm. potassium nitrate, and 1380 cc. water (total volume = four litres), was made up to a clear solution, and boiled down to about two-thirds bulk.   The initial boiling point was 129° C., rising finally to 141° C.   The solution was allowed to cool overnight, filtered by suction, and the crystals pressed and weighed, as was also the residual mother liquor.

Weight moist crystals	=	2792 gm.	Ratio of
Weight mother liquor	=	386 gm.	$NH_4NO_3 : KNO_3$
Therefore, wt. water evaporated	=	1194 gm.	= 7.25 : 1.

The mass of crystal was ground and mixed, and a sample analysed for potassium nitrate, ammonium nitrate, and moisture.

First experiment

Analysis of crystals

$$H_2O = 4.27\%$$
$$KNO_3 = 7.85\%$$
$$NH_4NO_3 \text{ (Kjeldahl)} = 88.08\%$$
$$\text{Ratio } NH_4NO_3 : KNO_3 = 11.2 : 1 \text{ by weight}$$

Analysis of mother liquor

$$KNO_3 = 4.52\%$$
$$NH_4NO_3 = 62.2\%$$
$$\text{Ratio } NH_4NO_3 : KNO_3 = 13.8 : 1$$

Second experiment

$$\text{Original solution } NH_4NO_3 = 2961 \text{ gm.}$$
$$KNO_3 = 592 \text{ gm.}$$
$$\text{Volume} = 4 \text{ litres}$$

This solution began to boil at 110° C. and was evaporated until the boiling point rose to 120° C.

$$\text{Wt. moist solid phase} = 1679 \text{ gm.}$$
$$\text{Wt. mother liquor} = 1898 \text{ gm.}$$

Analysis of crystals

H_2O	=	3.60%	Ratio $NH_4NO_3 : KNO_3$
KNO_3	=	19.00%	= 4.1 : 1.
NH_4NO_3	=	78.1%	
		100.7%	

Analysis of mother liquor

NH_4NO_3	=	56.58%	Ratio $NH_4NO_3 : KNO_3$
KNO_3	=	10.31%	= 5.5 : 1

The above agrees with the results of Caillart, and of Ando, and also of Allmand.

HOMOGENEITY OF SOLID SOLUTIONS PREPARED IN THE WET WAY
(BY CRYSTALLIZATION FROM AQUEOUS SOLUTION)

The solid solution containing 7.8% potassium nitrate was submitted to dilatometric investigation. It was found to transform, on cooling, at 21.6° C. Had such a preparation been homogeneous, it would not have transformed above 0° C. On repeating the experiment, transformation occurred at 12.6° C. It is noteworthy that this sample was prepared by boiling down a solution almost to dryness, i.e., the total mass of mixed crystals was much greater than the residual mother liquor. Under these circumstances it is perhaps not surprising that the product was not homogeneous. Accordingly a third preparation was made in the following manner:— A solution of original composition 48.8% ammonium nitrate and 11.48% potassium nitrate began to boil at 110° C., and was evaporated till the boiling point rose to 115° C. A crop of 303 gm. of crystals was obtained, and a mother liquor of 3550 gm. Analysis of these gave the following values:

Constituent	Crystals	Mother liquor
NH₄NO₃ , %	70.5	52.95
KNO₃ , %	27.2	11.34

This preparation showed no transformation between 40.6° and 0.8° C. Such a solid solution is, however, unnecessarily high in potassium nitrate. Accordingly, a fourth preparation was made by boiling down an original solution containing 43.95% ammonium nitrate and 5.115% potassium nitrate. Boiling began at 109° C. but no crystals were obtained up to 117° C. Further evaporation was continued to 119° C. Yields of 378 gm. of crystals and 1570 gm. of the mother liquor were obtained. The analyses were:—

Constituent	Mother liquor	Mixed crystals
NH₄NO₃ , %	57.92	87.2
KNO₃ , %	6.42	13.19

This preparation showed no transformation between 38.7° and 0.9° C.

Summary of Results

Owing to the nature of this work, which was dictated by practical considerations rather than any prearranged and systematic scheme, much of the discussion is necessarily included with the experimental results, and the reader is referred to that section. The main result of the work is that a solid solution of potassium nitrate in ammonium nitrate, containing, say, 5% potassium nitrate, can be kept indefinitely in form III (instead of the stable

form IV) at room temperature. Such a solid solution can be prepared by melting up the weighed components at the lowest possible temperature (about 175° C.), with stirring to ensure homogeneity. This homogeneous liquid is allowed to solidify and to cool to room temperature slowly. The resulting mass will show no discontinuous volume change between 0° and 100° C. It is quite insufficient merely to mix the potassium nitrate with the ammonium nitrate: the mass must be melted up (or crystallized from solution) to produce solid solution.

Solid solutions of potassium nitrate in ammonium nitrate can readily be prepared by crystallization from a mixed aqueous solution.

Below 0° C., the metastability is less pronounced. Even a solid solution containing as much as 10% potassium nitrate will eventually undergo transformation, if it is kept long enough at, say, −10° C., particularly if it is moist. On the other hand, the results of Professor Allmand with compressed blocks, according to which, on "cycling", i.e., alternately raising and lowering the temperature, the blocks undergo a progressive expansion, appear to us to be due to a disruption of the blocks, rather than to morphotropic change. In any case, the change III ⟶ IV is accompanied by contraction.

The effect of moisture in catalyzing the change has been demonstrated below 0° C.: above that temperature, it seems to be powerless to destroy the metastability.

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THE PORE STRUCTURE AND ADSORPTIVE PROPERTIES OF SOME ACTIVATED CHARCOALS

I. THE ADSORPTION OF WATER VAPOUR AND ITS DEPENDENCE ON PORE SIZE[1]

By M. N. Fineman[2], R. M. Guest[3], and R. McIntosh[4]

Abstract

An examination of the influence of the structure of charcoal adsorbents on the form of the water adsorption isotherm has been attempted by determinations of (1) surface areas of a series of charcoals of varying degrees of activation using nitrogen and butane as adsorbates; (2) total pore volume of each adsorbent sample by density measurements in helium and in mercury; (3) density of adsorbents when immersed in water; (4) adsorption isotherms for water vapour; and (5) surface areas of charcoals partly saturated with water vapour.

The evidence appears to suggest that certain very small and certain very large voids in charcoal are not occupied by water vapour at any value of the relative pressure. The former, 10% by volume, are important in terms of surface area; the latter, 30% by volume, influence pore volume calculations. An explanation of the shape of the water adsorption isotherm is attempted in the light of these facts. Estimates of the submicro, micro, and macro pore sizes show fair agreement when these are based upon either the capillary condensation theory or measurements of the total area and volume of the charcoal pores.

Introduction

When one considers the adsorptive properties of activated charcoal, it is at once apparent that the mechanism by which water vapour is taken up is in some way distinct from that for most other vapours and gases. In nearly every other instance the adsorption isotherm of the gas may be described analytically by an equation of the Langmuir type. In the case of water vapour, however, the form of the curve is that classified by Emmett and his associates as a Type V isotherm (9, pp. 1–36). In contrast with the Langmuir adsorption isotherm, very little adsorption is found at low values of relative pressure, and the greater part of the adsorption occurs over a narrow relative pressure range. Moreover, adsorption is not marked near saturation pressures, and the curve does not approach the weight axis asymptotically near a relative pressure value of 1 (20, pp. 143–154).

From the viewpoint of the Brunauer, Emmett, and Teller theory of multi-layer adsorption (6), such a curve is explained on the assumption that $E_1 < E_L$, where E_1 and E_L are the energy of adsorption in the first layer and the energy of liquefaction, respectively. The region near saturation must be explained on the assumption that all the voids have been filled, and that bulk condensation on the surface does not occur. On the other hand, the form of the curve may also be interpreted from the older conception of capillary condensation.

Here, too, certain regions of the isotherm are not easily reconciled with theory. In the first place, since the structure of the adsorbent may be expected to contain channels of dimensions ranging from those less than molecular dimensions to those of very large diameter, the extremely small amount of adsorption at low relative pressures would not be anticipated, unless the total volume of the small pores is negligible.   Near saturation a marked increase in amount adsorbed would be expected for an adsorbate whose wetting angle with the solid is zero.

In favour of the capillary condensation theory is the phenomenon of limited hysteresis.   It has been found by many observers that the adsorption–desorption curves for water do not correspond over a wide range of relative pressure.   Attempts to·explain this phenomenon by the presence of inert permanent gases (20, pp. 143–154), alteration of the wetting angle on desorption (1–4, 12), the form of the internal voids (19, Chap. XX, p. 1661), have frequently been made.   One of the most plausible of these has recently been put forward by Cohan (7, 8) on the assumption that condensation occurs along the walls of the interstices in an annular ring, while desorption occurs from a hemispherical meniscus.   These considerations alter the form of the equation relating condensation pressure and capillary radius by a factor of 2, which accounts for the hysteresis.

$$\text{Kelvin equation:} \qquad \ln \frac{P_r}{P_0} = \frac{-2\sigma\bar{v}\cos\theta}{rRT} \qquad\qquad (17)$$

$$\text{Cohan equation:} \qquad \ln \frac{P_r}{P_0} = \frac{-\sigma\bar{v}\cos\theta}{rRT} \qquad\qquad (7, 8)$$

where P_r is vapour pressure over capillaries of radius r,

$\quad P_0$ is vapour pressure at saturation,

$\quad \sigma$ is surface tension,

$\quad \bar{v}$ is molal volume,

$\quad \theta$ is angle of contact.

Important also is the deduction that no hysteresis will occur in voids whose diameter is less than four molecular diameters, for in this case the two equations will coincide.   This prediction has received some measure of confirmation from experiment, since the adsorption–desorption curves frequently coincide at relative pressures less than 0.4 (10).

It should be emphasized that, to our knowledge, no experiment has yet been devised that will serve to distinguish clearly between the various viewpoints. Nor has such an experiment been carried out in this investigation.   However, evidence has been accumulated that may be utilized in explaining the anomalies arising from the application of the capillary condensation theory.   In the first place, definite evidence is provided that certain of the voids of the adsorbent are not occupied by water at any value of the relative pressure. These voids appear to be of two types: very small in diameter and quite large in diameter.   The very small voids contribute little to the total pore volume

of the sample, but are of importance in terms of the surface area as measured by adsorption of nitrogen at liquid oxygen or liquid nitrogen temperatures. The large pores are relatively important from the standpoint of pore volume, but unimportant in terms of surface area. Water vapour is apparently adsorbed in voids of intermediate dimensions; this accounts for the narrow range of adsorption in terms of relative pressures. The fact that large pores do not fill up with adsorbate clearly suggests that the wetting angle between solid and adsorbed material is greater than zero. Somewhat similar views have been arrived at independently by Pierce and Juhola and their associates (23).

In this investigation a somewhat more careful examination of the influence of the structure of the adsorbent on the form of the adsorption isotherm has been attempted than in earlier work. The methods used were straightforward. They consisted of (*a*) determination of the total surface area of a series of charcoals of varying degrees of activity, using two adsorbates, nitrogen and butane (the latter was chosen to demonstrate the influence of molecular size); (*b*) determination of the total pore volume of each sample by measurements of the density of the adsorbent in helium and in mercury; (*c*) measurement of the density of the adsorbent when immersed in water; (*d*) determination of the adsorption isotherm for water; and, finally, (*e*) several preliminary determinations of surface area on charcoal samples partly saturated with water vapour.

Since the experimental procedures for most of these measurements are well known, they will not be described in detail. The procedure for determining (*c*) has been described fully in another paper of this series (11).

Experimental

(*A*) *Surface Areas*

The surface areas were measured by the method of Brunauer, Emmett, and Teller (6) in a standard type of adsorption apparatus. Except for Sample *G*, all samples showed monomolecular adsorption according to the criteria of the method. Using nitrogen, some were tested both at liquid oxygen and liquid nitrogen temperatures. The areas measured at the two temperatures agreed within the expected reproducibility of the measurements. The dead space of the adsorption cell was measured with purified helium at the temperature of the adsorption measurement, on the assumption that helium is not adsorbed to an appreciable extent (13, 14, 16). A standard procedure of preparing the charcoal sample was used throughout. It was evacuated at 110° C. until the pressure was between 10^{-4} and 10^{-5} mm. of mercury at that temperature with the pump shut off. No attempt was made to remove inorganic matter. Corrections for deviations from the ideal gas law were applied in all the adsorption experiments.

(*B*) *Determination of the Density in Helium*

The experimental arrangement for determining the density in helium was almost exactly similar to that of Howard and Hulett (15). Evacuation of the

samples was carried out as described above, and purified helium was employed. No drift in the density value with time was observed if the purification was properly carried out, a result that does not agree with the observation of Howard and Hulett on the carbons employed by them.

(C) *Determination of the Density in Mercury*

The density of the samples in mercury was readily determined by means of a pycnometer arranged so that after evacuation the volume of a known weight of carbon could be read directly on a burette as the difference between the volume of the container when empty and when partially filled by the carbon sample. The final volume reading was made under conditions such that the pressure of mercury on the sample was approximately $\frac{1}{2}$ atm. Since mercury may be forced into the larger voids by pressure, a small error is introduced by this method of measurement. However, similar determinations in a different form of apparatus where the effective pressure of mercury is approximately $1\frac{1}{2}$ atm. (22) shows that this error is less than 3 to 5%.

(D) *Determination of the Density in Water*

The density of the samples in water was found in a special form of pycnometer (11). The carbon was thoroughly evacuated before being wetted, and the equilibrium value of the density determined.

(E) *Water Adsorption Isotherms*

The water adsorption at 20° C. was determined by the gain in weight of the sample after equilibrium had been established between the sample and a sulphuric-acid–water solution of known density. Evacuation of the sample was carried out as previously described. The sulphuric-acid–water solutions were freed of gases by repeated freezing and evacuation. The density of the solution was determined after equilibrium with the samples had been attained. The adsorption balance was similar to that of McBain and Bakr (21), except that the spiral was made of 32 gauge phosphor-bronze wire. The spirals were about 8 cm. long and 0.4 cm. in diameter, with about 40 turns per cm. The calibration of the spiral was determined after the evacuation at 110° C. to correct for possible deformation when heated under strain. The reproducibility of the measurements was less than would be expected from the sensitivity of the spirals. This may have been due to variations in the thermostat control or to the length changes that would be caused by fluctuations in room temperature, since an appreciable length of the spiral system was above the thermostat liquid level. With measurements reproducible to 0.005 cm. on the cathetometer, these spirals could support about 10 gm. without exceeding their elastic limit. On the average, 1 gm. weight caused an extension of about 2.5 cm. Despite temperature variations, the values indicated are believed sufficiently accurate, so that the comparisons that are made later are substantially correct.

Limited hysteresis of the water isotherms was found with these samples. No thorough examination of the hysteresis loops was attempted, and the data are therefore not included. The existence of hysteresis, as emphasized

in the introduction, is most readily explained on the basis of the capillary condensation theory.

(F) Carbon Samples

The carbon samples A to F, inclusive, were made by the steam activation of cocoanut shell at the Standard Chemicals Co. Ltd., Montreal. The samples were obtained from a single furnace charge. A grab sample of the charge was taken at intervals of 12 hr. The grab sample was then screened and material of 8 to 14 mesh collected for study. The ash content of these materials is approximately 0.5% (22).

Sample G is a zinc chloride activated material obtained from the National Carbon Company. The ash content of this sample is about 2%. If volatilization of zinc chloride occurs during the combustion test, the amount of inorganic material in the untreated sample will be somewhat greater than this figure (22).

Results

Surface Areas

The surface areas of the samples using both butane and nitrogen are given in Tables I and II. The Langmuir form of adsorption isotherm is clearly

TABLE I

AREA AVAILABLE TO NITROGEN AT 90.1° K.

Sample	Time in furnace, hr.	v_m* cc./gm.	Surface area, sq. m./gm.	$(E_1 - E_L)$	E_1
				Kcal. per mole	
A	12	14_0	64_4	0.8_9	2.2_2
B	24	16_3	74_9	0.9_5	2.3_8
C	48	19_5	89_5	0.8_6	2.1_9
D	72	20_1	96_3	0.9_7	2.2_9
E	96	23_3	107_0	0.8_8	2.2_1
F	120	24_7	113_6	0.9_1	2.2_4

*v_m is the volume of adsorbate that covers the surface with a monolayer.

TABLE II

AREA AVAILABLE TO BUTANE AT 0° C.

Sample	v_m cc./gm.	Area (a)*	Area (b)**	$(E_1 - E_L)$	E_1
		Sq. m./gm.		Kcal. per mole	
A	$38._3$	33_3	50_0	2.0_0	7.3_0
B	$48._0$	41_7	62_5	2.0_0	7.3_0
C	$63._6$	55_3	82_9	2.1_0	7.4_0
D	$69._3$	60_2	90_3	2.1_9	7.4_9
E	$80._9$	70_3	105_0	2.1_0	7.4_0
F	$84._9$	73_7	110_0	2.2_6	7.5_6

* Area (a). Butane molecular area = 32.1 sq. Å.
** Area (b). Butane molecular area = 48.0 sq. Å.

shown by the linearity of the plots in Figs. 1 and 2.   An area of 17.0 sq. Å is
assumed for nitrogen at 90° K. and 16.2 sq. Å at 77° K.   For the butane
adsorption at 0° C. two values for the area of the butane molecule have been
used, because of the uncertainty concerning its accuracy (10).   These values
are 32.1 sq. Å and 48.0 sq. Å, respectively.

To show the influence of the size of the adsorbate molecule on the deter-
mined area, the ratio of the area values obtained using nitrogen to those
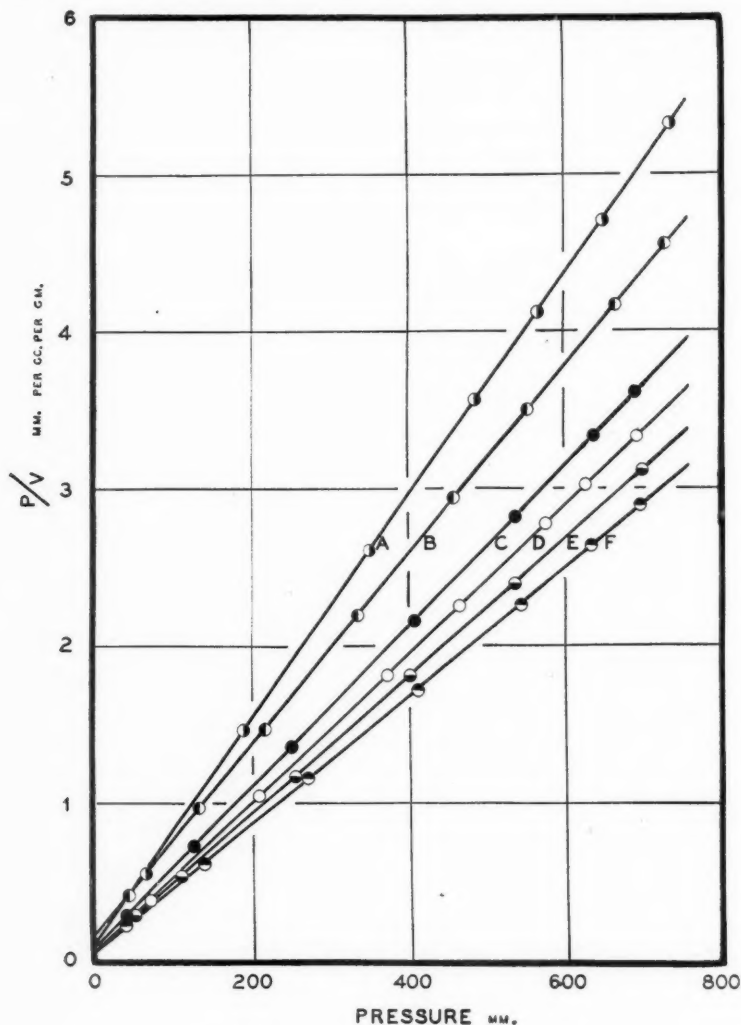
FIG. 1.   *Langmuir plot for nitrogen isotherms.*
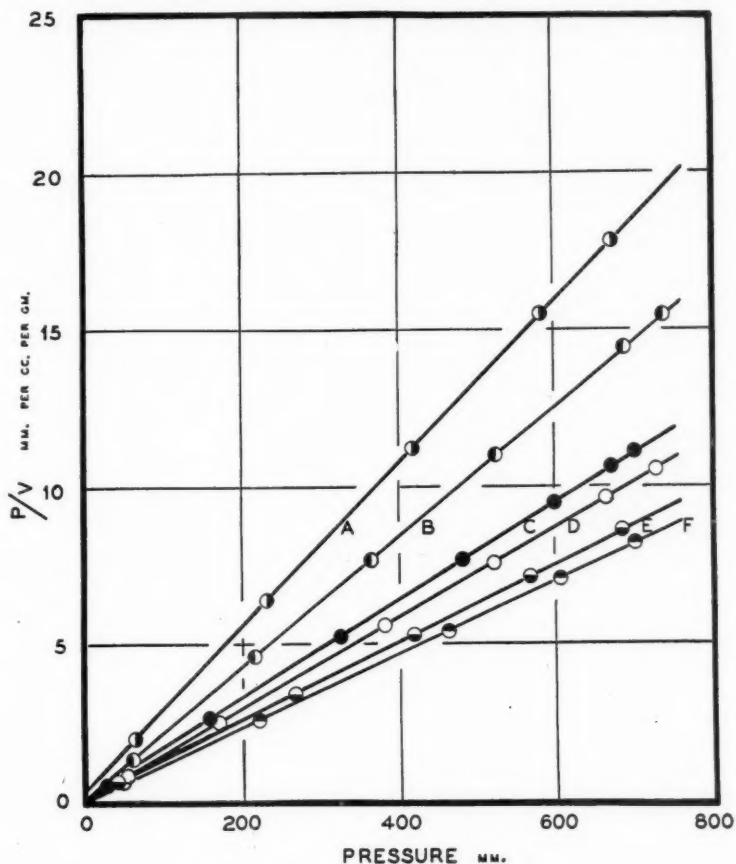
FIG. 2. *Langmuir plot for butane isotherms.*

obtained using butane are given in Table III. It is clear from these results that certain portions of the surface that are available to the nitrogen molecule are not available to the butane molecule in the less highly activated members of the series. Moreover, if the correct area for the butane molecule is 32.1 sq. Å this statement applies to all members of the cocoanut shell series. Such an explanation of the results seems indicated, since the calculated energy of adsorption remains virtually constant for both adsorbates throughout the series. From the dependence of the amount of adsorption on the size of the adsorbate molecule, one is led to expect a mean pore radius for these samples of the order of molecular dimensions.

Pore Volumes and Mean Pore Radii

The values of the density in helium and in mercury are given in Table IV. From the reciprocals of these values, the total pore volume of each sample is

calculated and included in the table. It is assumed in making this calculation that the helium molecule is sufficiently small to penetrate the entire structure and that mercury does not penetrate the structure to an appreciable extent.

TABLE III

APPARENT STERIC FACTOR

Sample	Ratio of areas $\frac{\text{nitrogen}}{\text{butane}}$	
	Butane area (a)	Butane area (b)
A	1.9_3	1.2_9
B	1.7_9	1.2_0
C	1.6_2	1.0_8
D	1.6_0	1.0_6
E	1.5_2	1.0_2
F	1.5_4	1.0_3

TABLE IV

DIRECT PORE VOLUME DATA

Sample	Charcoal density, gm./cc.		Pore volume, cc./gm.
	Helium	Mercury	
A	1.98	1.09_9	0.41
B	2.01_5	1.08_5	0.42
C	2.02_2	1.01_8	0.49
D	2.03_7	0.97_4	0.54
E	2.05	0.95_4	0.56
F	2.07	0.89_1	0.64
G	1.96	0.53_5	1.33

It will be observed that a marked increase in the pore volume is brought about by the activation process. In the same way a very large increase in the surface area was shown by the data in Tables I and II. If now the voids of the particles are assumed to approximate cylinders in their form, a value of the mean pore radius may be calculated from a knowledge of the pore volume and the surface area, using the relation

$$V/A \ = \ r/2$$

where V is the pore volume per gm.

A is the surface area per gm.

r is the mean pore radius.

These values are given in Table V. Both molecular areas for the butane molecule have again been employed. It is interesting to note that the mean radius calculated from the nitrogen area is approximately constant for the cocoanut shell carbons, and somewhat larger for the zinc chloride activated sample (G). The larger value of the mean pore radius for this sample would

be anticipated from the water adsorption isotherm, since the relative pressure at which one-half of the moisture saturation value has been adsorbed is greater than for the cocoanut shell carbons (22). The value for the cocoanut shell series is about 11 Å.

TABLE V

Pore radii data

Sample	Radius in $Å$ using $r = 2V/A$		
	Nitrogen area	Butane area (a)	Butane area (b)
A	12.7	24.6	16.4
B	11.2	20.1	13.4
C	11.0	17.7	11.8
D	11.2	17.9	12.0
E	10.5	16.0	10.7
F	11.2	17.4	11.6
G	14.8	—	—

Water Adsorption Data

The adsorption isotherms for five of the cocoanut shell samples are represented in Fig. 3. Pertinent data from these isotherms are given in Table VI. The relative pressure of water vapour at which one-half of the saturation value of moisture content has been adsorbed is given for each sample. The mean

TABLE VI

Water adsorption data

Sample	Relative pressure at 50% moisture saturation value	Pore radius by Cohan eqn., $Å$	Max. wt. adsorbed, gm./gm.	Pore volume by H_2O adsorption, cc./gm.	Ratio of pore volume filled by H_2O at saturation to total pore volume
A	0.51	8.0	0.20_8	0.20_8	0.50
B	0.51	8.3	0.22_0	0.22_0	0.52
C	0.54	8.7	0.31_5	0.31_5	0.64
E	0.57	9.5	0.37_0	0.37_0	0.66
F	0.59	10.0	0.44_1	0.44_1	0.69
G	0.72	16.2	0.93_5	0.93_5	0.70

pore radius calculated from this pressure by means of the Cohan equation (wetting angle assumed to be zero) is also given. The good agreement between the mean radius estimated by this method and that given previously is striking. It must be considered as partially fortuitous, however, in view of the direct evidence that only about 60% of the total pore volume is filled by water. This is illustrated in the last column of the table, where the volume filled by water is compared with the total volume. In making this comparison it has
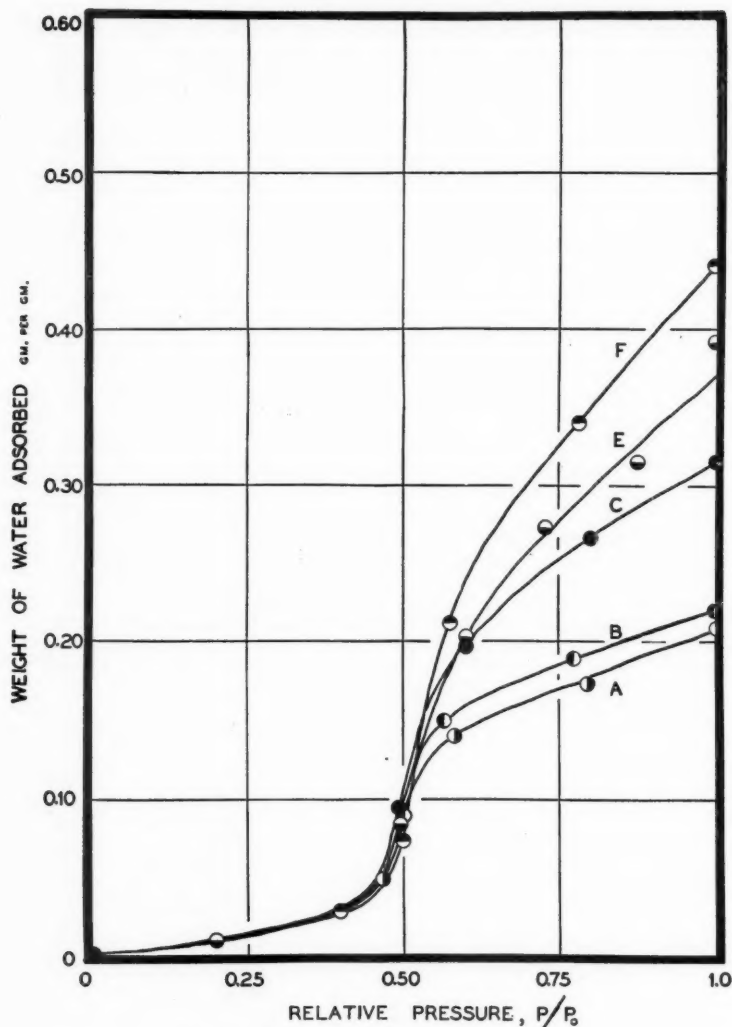
FIG. 3. *Water sorption on charcoal at 20.0° C.*

been assumed that the density of the adsorbed water may be taken as unity without serious error. This assumption has now been verified (22). Further, the value of the wetting angle has been assumed to be zero, which is apparently not justified by the form of the isotherm near saturation. Use of the Kelvin equation doubles the calculated mean pore radius.

In Table VII the area wetted by water is compared with the area determined by the Brunauer, Emmett, Teller method using nitrogen. The evalua-

TABLE VII

SURFACE AREA DATA FROM WATER ADSORPTION ISOTHERMS

Sample	Area, sq. m./gm.			Ratio $\dfrac{water}{nitrogen}$
	Nitrogen	Water	Free	
A	64_5	50_8	13_7	$78._8$
B	74_9	55_4	19_5	$74._0$
C	89_5	69_6	19_9	$77._8$
E	107_1	74_8	32_3	$70._0$
F	113_6	84_0	29_6	$74._0$

tion of the area wetted by water required the assumption of cylindrical voids and a zero wetting angle. With these assumptions the area may be evaluated by integration of the equation

$$A = 2 \int_{w \text{ at } P}^{w \text{ at } P_0} \frac{RT . \ln \dfrac{P_0}{P}}{\bar{v} . \sigma} \cdot dw$$

(where w is weight of water adsorbed at a given vapour pressure) in a manner similar to that suggested by Kistler, Fischer, and Freeman (18) except that no correction has been applied for monomolecular adsorption. From the form of the isotherm it is apparent that little error can be introduced by this omission. Had the desorption isotherms been determined, an evaluation of the area by their method could have been made without assumptions as to the structure of the internal voids. Since this method applies strictly only to the desorption isotherm, the assumption of cylindrical voids and use of the Cohan equation were required with our data.

Nitrogen Adsorption on Moist Carbons

In Tables VIII and IX preliminary data on the surface areas of partially wetted carbons are given. Fig. 4 illustrates certain of the isotherms obtained from such systems. The Langmuir type of adsorption curve is again found.

The deductions from these determinations are given in the general discussion.

TABLE VIII

AREA OF WET CHARCOAL AVAILABLE TO NITROGEN AT 90.1° K

Sample *F*

Rel. press. water vap., P/P_0	Weight water adsorbed, gm./gm.	v_m, cc./gm.	$(E_1 - E_L)$	E_1	Specific surface, sq. m./gm.	Percent of total surface
			Kcal./mole			
0.0	0.0	24_7	0.9_1	2.2_4	113_6	100.0
0.47	0.05	22_4	0.9_3	2.2_6	103_0	90.6
0.87	0.38	$14._5$	1.0_4	2.3_7	6_8	5.9

TABLE IX

Nitrogen adsorption data at 77.3° K.

Sample	Water content	n^*	v_m, cc./gm.	Surface area, sq.m./gm.	c^{**}	$(E_1 - E_L)$	E_1
						Kcal./mole	
F	Dry	1.0	26_9	118_0	$94._2$	0.7_0	2.0_4
G	Dry	1.8	42_0	184_1	23_9	0.8_5	2.1_8
G	Sat'd	2.0	$32._4$	14_2	30_9	0.8_9	2.2_2

* n is number of adsorbed layers.

$^{**} \ln c = \dfrac{(E_1 - E_L)}{RT}$.

Discussion

The chief points of interest in the preceding data are: (1) the agreement between the mean pore radius determined by the two methods; and (2) the evidence that shows that only part of the internal volume of the carbon is utilized in the adsorption of water vapour.

The voids of an adsorbent are frequently classified according to their apparent sizes as submicro pores, micro pores, and macro pores (5, pp. 374–377). By employing the data already presented, and by considering the values of the density of each sample when immersed in water, an attempt may be made to determine the role played in the adsorption of water vapour by these three ranges of pore size.

From the pore volume filled by water vapour at saturation and from the pore volume measured directly, it is apparent that a large number of the voids do not fill with water vapour even at saturation. If the density of the carbons when immersed in water is also considered, a very small volume of approximately 0.05 cc. per gm. is seen to be unoccupied by water even under these conditions of complete immersion and one atmosphere pressure on the liquid. These voids into which liquid water will not penetrate are considered to be the submicro pores, and from the relative pressure at which adsorption of water vapour begins we are led to conclude that the submicro pores are of radius less than 6 Å. They represent only about 10% of the total pore volume, but because of their narrow radius will have a relatively large surface compared with larger pores.

It is clear also that since the volume filled by water at saturation plus the volume of the submicro pores does not equal the total pore volume, some larger pores remain unfilled up to relative vapour pressures very close to one. This is to be expected from the form of the adsorption curve near saturation, and from the finding that, even after the equilibrium saturation value of moisture content has been attained, a capacity to adsorb other vapours still exists. This residual unfilled volume is considered to be that due to the macro pores, and as may be seen from the figures in Table X is about 30% of the total pore volume. Because of the relatively large diameter of these voids they are of lesser importance in terms of area than the smaller ones.
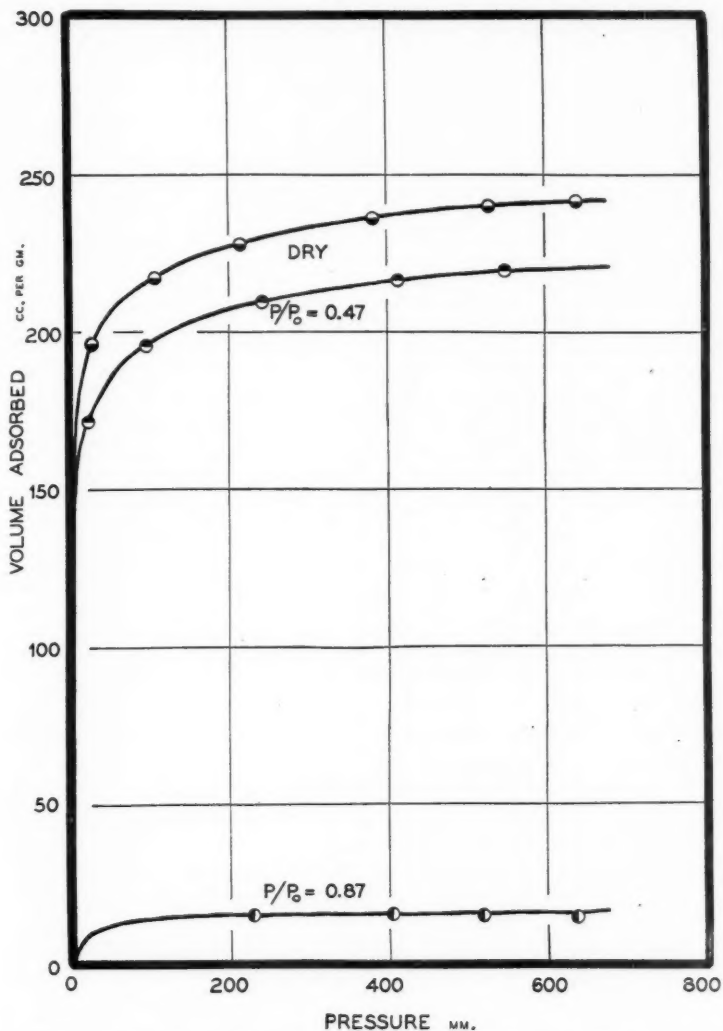
FIG. 4.   *Nitrogen adsorption on Sample F in equilibrium with water vapour at 90.1° K.*

A semiquantitative check of these statements may be made with the data of Table VIII for Sample *F*.   The total surface area of the dry carbon was measured as 1136 sq. m. per gm.   After equilibrium had been established between the sample and a solution of 0.87 relative pressure of water vapour, the residual surface area available to nitrogen was determined and was found to be 66 sq. m. per gm.   If the submicro pore volume is blocked off by the water adsorption (22), then the 66 sq. m. per gm. is the surface area of the

TABLE X

Free volumes

Sample	Density, gm./cc.		Sub-micro vol., cc./gm.	Direct pore vol., cc./gm.	Water at sat'n., gm./gm.	Free vol. at sat'n., cc./gm.		Water at 0.87, gm./gm.	Free vol. at 0.87, cc./gm.	
	H_2O	He				Total	Macro		Total	Macro
A	1.82	1.98	0.05	0.41	0.21	0.20	0.15	0.19	0.22	0.17
B	1.84_6	2.01_3	0.04	0.42	0.22	0.20	0.15	0.20	0.22	0.17
C	1.85_9	2.02	0.04	0.49	0.31	0.18	0.14	0.28	0.21	0.17
E	1.86_2	2.05	0.05	0.56	0.37	0.19	0.14	0.32	0.24	0.19
F	1.86_2	2.07	0.06	0.64	0.44	0.20	0.15	0.38	0.26	0.21
G	1.71	1.96	0.08	1.33	0.94	0.39	0.31	—	—	—

macro pores that are not filled at a relative pressure of 0.87. From Table **X** the volume of the macro pores is seen to be 0.21 cc. per gm. By application of the Cohan equation, the smallest pore radius into which water vapour will not condense at this relative pressure is 38 Å. The surface area associated with these larger pores may be calculated on the assumption that all are of this radius. This is not strictly correct, of course, since some will undoubtedly be larger in radius with consequent reduction of the area value. The calculated area, assuming cylinders as an approximation, is $A = 2V/r = 110$ sq. m. per gm. as compared with 66 sq. m. per gm. by experiment.

By a similar process the mean radius of the submicro pores may be estimated. Of the original surface (1136 sq. m. per gm.) about 58%, or 660 sq. m. per gm., is wetted by water at the relative pressure of 0.87. Experiment has shown that the area of the macro pores is 66 sq. m. per gm., leaving about 410 sq. m. per gm. as the area associated with the submicro pores, whose volume is 0.06 cc. per gm. The mean radius of these pores is given by $r = 2V/A = 3.0$ Å approximately. Sufficient data for other samples have not yet been obtained to test these calculations further. The agreement is extremely good, however, when one considers the numerous assumptions made, concerning the form of the voids, in the theory of the surface area measurements and in the capillary condensation theory calculations.

Conclusions

It appears that fair agreement concerning the mean pore size of an adsorbent such as activated charcoal may be obtained when these estimates are based upon either the capillary condensation theory or measurement of the total area and volume of the pores. It is also apparent that only the micro pores of the carbon are involved in the adsorption of water vapour. The submicro pores are inactive for reasons not yet clarified, while the macro pores, although readily wetted when immersed in water, do not adsorb the vapour even near saturation pressure. An estimate of the radius of the submicro pores may be made by application of the Cohan equation or by a knowledge of their volume and associated area. The same may be done for the macro pores, provided

that measurements of area available to nitrogen on partially wetted carbons are made. Finally, to assess the behaviour of the carbon, a knowledge of pore volume, density in water, surface area, and the adsorption isotherm for water vapour are all required.

Acknowledgment

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THE PORE STRUCTURE AND ADSORPTIVE PROPERTIES OF SOME ACTIVATED CHARCOALS

II. THE APPARENT DENSITY OF CHARCOAL IN LIQUID MEDIA[1]

By R. M. Guest[2], R. McIntosh[3], and A. P. Stuart[2]

Abstract

The apparent density of eight charcoal samples has been determined in a series of liquids at two temperatures, 25° and 55° C. From the data a correlation between apparent density of the charcoal and surface tension of the measuring fluid is suggested. An attempt is made to explain this approximate regularity in terms of the surface free energy change on immersion.

It has been demonstrated by several investigators that the apparent density of activated charcoal or silica gel depends upon the displacement medium in which the measurement is made (7, 8, 9, 13). The causes of this are, however, still not clearly established. Recently Brunauer (5) has reviewed both the experimental evidence and the explanations that have been advanced. Cude and Hulett (7) have suggested that the differences of density may be attributed to the proportion of the total internal volume of the porous material that is filled. This view is supported by the fact that the density measured in helium is always greater than that observed in any other fluid (14). If helium is not adsorbed to an appreciable extent at the temperature of the experiment, the density in helium must be the true density, and the lower values exhibited in other media are then due to incomplete penetration into the porous structure.

Harkins and Ewing (13), noting that the greater densities were obtained in liquids of large compressibility, suggested that compression of the liquid film at the solid–liquid interface could account for the large apparent densities. They rejected the explanation of penetration since no correlation was apparent between the measured density and the ratio of the surface tension to the viscosity of the liquid. Since, for an equilibrium measurement, the viscosity of the liquid could hardly be involved, the lack of a correlation is not relevant. Moreover, the very large compressional forces (of 10,000 atm. and greater) calculated from this theory tend to discredit such an explanation as does the deduced value 1.6 gm. per cc. for the true density of activated carbon.

Culbertson and his collaborators (8, 9) have recently extended the experimental data by comparing the behaviour of charcoal and silica. They have reported, for example, that silica has a higher density in water than has charcoal, while in petroleum ether silica has the lower density. From such evidence

they have concluded that both the extent of penetration and the amount of compression may be involved, and that the forces between the solid surface and the liquid cannot be neglected.

Culbertson and Weber (9) have pursued the study further and have corroborated in the case of charcoal the apparent dependence of density on the compressibility of the fluid as first noted by Harkins and Ewing (13). This regularity did not hold for silica, however, and other factors such as dipole moments were examined in an attempt to explain the differences.

A different basis of correlation is suggested here. It has been attempted since no explanation had been advanced to account for differing degrees of penetration into the porous structures, even if that factor alone were the cause of the varying density values. Two possible reasons for a variation in degree of penetration come to mind. First, the size of some of the internal voids may be too small to permit the entrance of certain liquids. Emmett and his associates (10) have clearly established that this factor is of real importance in adsorption, and that the size of the adsorbate molecules influences the value of the surface area of the adsorbent when measured by physical adsorption. As an extreme case may be cited the behaviour of certain forms of chabasite which do not adsorb large molecules, but which have an appreciable capacity to adsorb substances whose molecules are small. Since with activated charcoal the mean pore radius is relatively small (11, 16) (of the order of 15 Å for the materials studied here), it is probable that molecular size may be of importance.

Another factor may also be operative. The free energy change on "immersional wetting" is usually considered as $\sigma_{sv} - \sigma_{sl}$, where σ_{sv} is the surface free energy of the solid–vapour interface and σ_{sl} the surface free energy of the solid–liquid interface (4). If, on immersion, conditions are such that a large change in area of the liquid–vapour interface occurs, "immersional wetting" becomes similar to "spreading wetting", and σ_{lv}, the surface free energy of the liquid–vapour interface, may be of paramount importance. Marked extension of the liquid–vapour interface will occur on immersing porous bodies, provided that the contact angle of solid–liquid is not zero. Only when this angle is zero does the free energy change

$$-\Delta F_s = \sigma_{lv}(\cos \theta - 1),$$

(where θ is the angle of contact between solid and liquid) permit spontaneous wetting. That the wetting angle between charcoal and many liquids is not zero is suggested by the form of the adsorption isotherm at saturation pressures, since the isotherm does not become asymptotic to the weight axis as a relative pressure of one is approached (12, p. 220). It follows therefore that work must be done on the system to bring about complete wetting, and, since very large surface areas are involved when dealing with activated charcoal, it is suggested that both the surface tension of the liquid and the wetting angle determine the degree of penetration when the wetting angle is not zero. Unfortunately, the determination of the wetting angle does not

appear feasible and an attempt to correlate density values with σ_{lv} only has been possible.

In order to examine whether such factors as molecular size and surface free energy of liquid–vapour were influential in determining the density of charcoal, eight samples were studied in a variety of liquids. The liquids were chosen primarily because of their surface tensions, and variations of the constituent atoms or their arrangement in a regular manner was not attempted. The charcoals were chosen in the hope that a wide range of the ratio of internal volume to area would be exhibited, and thus a critical test of the compressibility theory might be attempted. However, the determination of the volume and area values, which was carried out concurrently, revealed that their ratio did not change materially.

Circumstances prevented the accumulation of similar data on several samples of silica gel, although measurements of the same type as with charcoal were begun, and no comparison of the two substances using the techniques described below is available.

Experimental

A. Charcoal

The charcoal samples consisted of seven materials made from cocoanut shell carbon and one zinc chloride activated material. The cocoanut shell carbons were obtained from the Standard Chemicals Co. Ltd., Montreal, and consisted of one series of six samples removed from the activator at approximate intervals of 24 hr., and one fully activated sample. These materials therefore represent products from a common source and common activation process, but of varying adsorptive capacity. The zinc chloride activated material, obtained through the courtesy of the National Carbon Company, was chosen in the hope that it would possess a relatively large volume-to-area ratio.

B. Pore Volume and Surface Area Measurements

The total pore volume of each sample was measured by determining its density in helium and in mercury (11). The apparatus and method used in finding the helium density were essentially the same as those reported by Howard and Hulett (14) and have already been sufficiently described (11). The assembly in which the density in mercury was found has also been reported in the earlier publication (11). The measurements of surface area were made using the method of Brunauer, Emmett, and Teller (6) employing nitrogen at liquid air temperature, and the values have already been reported (11).

C. Determination of the Density in Various Liquids

The pycnometer used to measure the densities in the liquids was of the following design. A piece of 15 mm. Pyrex tubing was sealed to an ordinary type of pycnometer just below the ground glass opening of the pycnometer. A side-arm was then sealed to this connecting tube, and a constriction made in the side-arm, which was bent as shown in Fig. 1, to facilitate its immersion

in the liquid. A fragile tip was made on the side-arm.   The charcoal sample was placed in the pycnometer bulb and the whole assembly sealed to an evacuating system through the 15 mm. Pyrex tube. About eight such
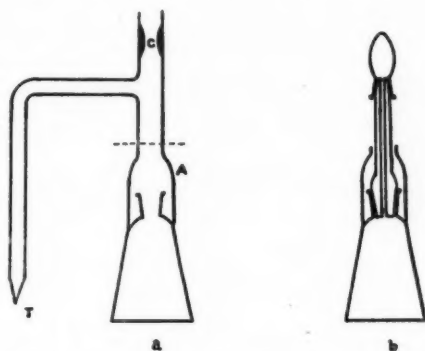
FIG. 1.   *Pycnometer for measuring apparent density of charcoals.*

assemblies were then surrounded by an air-bath maintained at 110 $\pm$ 5° C. and the charcoal thoroughly evacuated at this temperature. When the pressure over the charcoal had fallen to between 10^{-4} and 10^{-5} mm. of mercury at 110° C., the connecting tubes were carefully sealed off, with the pumps operating.   The pycnometer bulb, connecting tube, and charcoal were then weighed.   The tip of the side-arm was next broken under the surface of the liquid, and the charcoal wetted.   Next, the connecting tube was broken at the approximate position of the dotted line of Fig. 1, and the pycnometer capillary inserted in the ground glass neck.

The only difficulty encountered when using this type of pycnometer was in freeing the space between the connecting tube and the pycnometer neck of liquid.   This was achieved by blowing the space out thoroughly with dried air.

D. Purification of Wetting Liquids

The liquids employed were reagent grade materials, except the nitrobenzene, which was purified by fractional crystallization, followed by vacuum distillation.   Ordinary distilled water was employed in making determinations with water.   All liquids were degassed by boiling under reduced pressure just before use.   Non-aqueous materials were kept dry by storage over Drierite.   When making measurements with glycerine and with ethylene glycol the pycnometers were placed in closed containers with Drierite present, and the containers then placed in the thermostats.

E. Establishment of Equilibrium Values

In order to ensure that the determined density values should be as free as possible from errors, the time required to establish a constant density value was first investigated.   Benzene, ethyl acetate, and pyridine were used in this test, and the weights of the pycnometers containing charcoal and these

liquids followed until no further changes were observed. The pycnometers were then taken from the thermostat operating at $25 \pm 0.01°$ C., and placed in a thermostat operating at $55 \pm 0.01°$ C., and changes were again followed until they became negligible. The vessels were then replaced in the 25° C. bath and again examined. This procedure was repeated until the density value obtained at either temperature was constant. Typical data are given for ethyl acetate in Table I, and are represented for the three substances in Fig. 2.

TABLE I

VARIATION OF APPARENT DENSITY WITH TIME

Time, days	Pycnometer (bottom) charcoal + ethyl acetate, gm.	Temperature, °C.	Density, gm./cc.
1	85.825	25	2.05
2	85.852		2.06
4	85.868		2.06_9
5	85.872		
6	85.874		
7	85.875		2.07_2
10	84.563	55	
11	84.564		
12	84.566		2.09_4
14	84.578		
15	84.583		2.10_1
16	84.586		
20	84.588		2.10_3
21	85.909	25	
22	85.908		
23	85.908		
24	85.912		
25	85.912		2.08_8
31	84.590	55	2.10_6
34	84.593		
36	84.592		
38	84.592		
39	84.595		
40	84.595		
41	84.594		2.11
42	85.911	25	
43	85.910		
47	85.915		
48	85.914		
49	85.914		2.09
50	84.594	55	
51	84.590		2.11
52	85.916	25	
53	85.917		
54	85.914		
85	85.915		
86	85.915		2.09

It was thus established that drifts were not appreciable after 30 to 40 days, and the practice was adopted of allowing the pycnometers to stand at a given temperature for about 30 days before being weighed.   If then significant changes were not observed over a period of a week (temperatures were varied if the boiling point of the liquid permitted) the values were taken as equili-
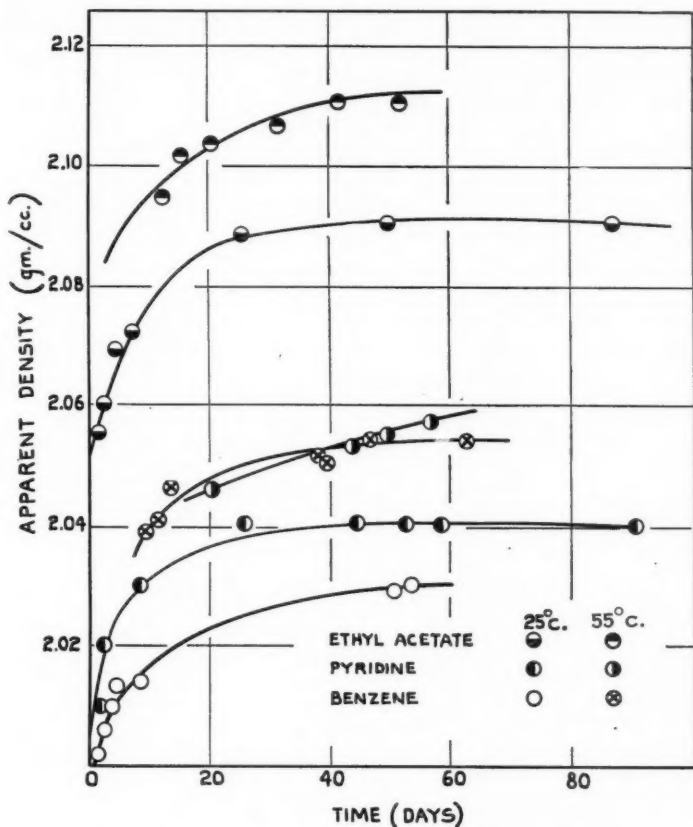
FIG. 2.   *Illustration of rate of attainment of equilibrium in density determinations.*

brium values.   From the initial rate of drift it appears doubtful whether determinations of density after two hours, as performed by Culbertson and Dunbar and Weber (8, 9), are significant where small differences in density are observed.

The variation of the temperature of measurement was also useful in testing the relation between density and surface tension, and two temperatures were always employed where feasible.

F. Expansion of the Solid

The investigations of McBain, Porter, and Sessions (15) and Bangham and Razouk (3) have shown that porous adsorbents such as charcoal swell when vapours are adsorbed. Changes in volume of the adsorbent also occur when the solid is immersed in the liquid. This correction factor for the density has apparently not been applied by earlier workers, nor has it been applied in this investigation. From the data obtained in adsorption studies it appears that the expansion is small, about 0.5% at saturation pressure for methyl alcohol and is about the same order for all adsorbates. No serious error is to be expected in the general nature of the results given below owing to this omission.

Results

The complete data for the cocoanut shell sample which had been fully activated (*S.B.T.* No. 95) are given in Table II. Similar data for the zinc

TABLE II

SUMMARY OF APPARENT DENSITY DATA FOR *S.B.T.* 95

Liquid	25° C.		55° C.	
	Surface tension, dynes/cm.	Density of charcoal, gm./cc.	Surface tension, dynes/cm.	Density of charcoal, gm./cc.
Water	72.0	1.90$_7$	67.0	1.88$_6$
Glycerine	63.0	1.96$_3$	61.0	1.95$_6$
Ethylene glycol	47.0	1.94$_5$	44.5	1.93$_5$
Nitrobenzene	43.3	2.01$_2$	39.8	2.02
Pyridine	37.1	2.04	32.9	2.05$_1$
Chlorobenzene	32.5	2.04$_6$	29.0	2.05$_3$
Carbon disulfide	31.4	2.07$_3$		
Xylene	29.6	2.04$_6$	26.2	2.06$_3$
Benzene	28.2	2.03$_1$	24.4	2.05$_3$
Toluene	27.9	2.04$_9$	24.3	2.06$_7$
Chloroform	26.4	2.04$_8$		
Carbon tetrachloride	26.3	1.94$_5$	22.6	1.96$_7$
Ethyl acetate	23.3	2.09$_1$	19.7	2.11
Acetone	23.3	2.12		
Methyl alcohol	22.4	2.07$_6$	19.8	2.09$_1$
Ethyl ether	16.4	2.12$_6$		
Pentane	14.8	2.11$_3$		

chloride activated sample (*C.W.S.N.* 178 *B*-2) are given in Table III. These data are also plotted against the value of the surface free energy liquid–vapour of the liquids (Figs. 3 and 4) which were chosen, as stated above, to achieve as wide a variation of this property as possible. Surface free energy values were obtained from the International Critical Tables.

Data obtained with the six samples of the series of cocoanut shell carbons of various periods of activation (Samples *A* to *F*) are given for 25° C. in Table IV and 55° C. in Table V. The total pore volume and the fraction of

TABLE III

SUMMARY OF APPARENT DENSITY DATA FOR *C.W.S.N.* 178 *B-2*

Liquid	25° C.		55° C.	
	Surface tension, dynes/cm.	Density of charcoal gm./cc.	Surface tension, dynes/cm.	Density of charcoal, gm./cc.
Water	72.0	1.70$_9$	67.0	1.68$_9$
Pyridine	37.1	1.86$_2$	32.9	1.87$_4$
Chlorobenzene	32.5	1.88	29.0	1.89$_2$
Benzene	28.2	1.84$_9$	24.4	1.87$_5$
Carbon tetrachloride	26.3	1.85$_1$	22.6	1.87$_2$
Ethyl acetate	23.3	1.88$_6$	19.7	1.91$_3$
Ethyl ether	16.4	1.93$_7$		

FIG. 3.   *Apparent density of charcoal sample S.B.T. 95 as function of the surface tension of the liquids.*

TABLE IV

APPARENT DENSITIES OF PROGRESSIVELY ACTIVATED SAMPLES IN SEVERAL LIQUIDS
AT 25° C.

S.B.T. No. 72   Density, gm./cc. $T = 25°$ C.

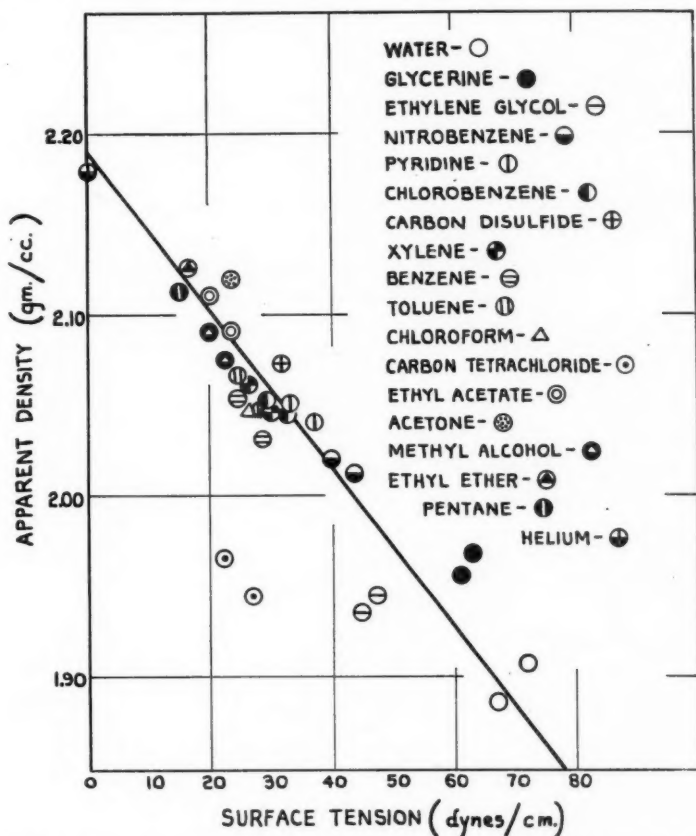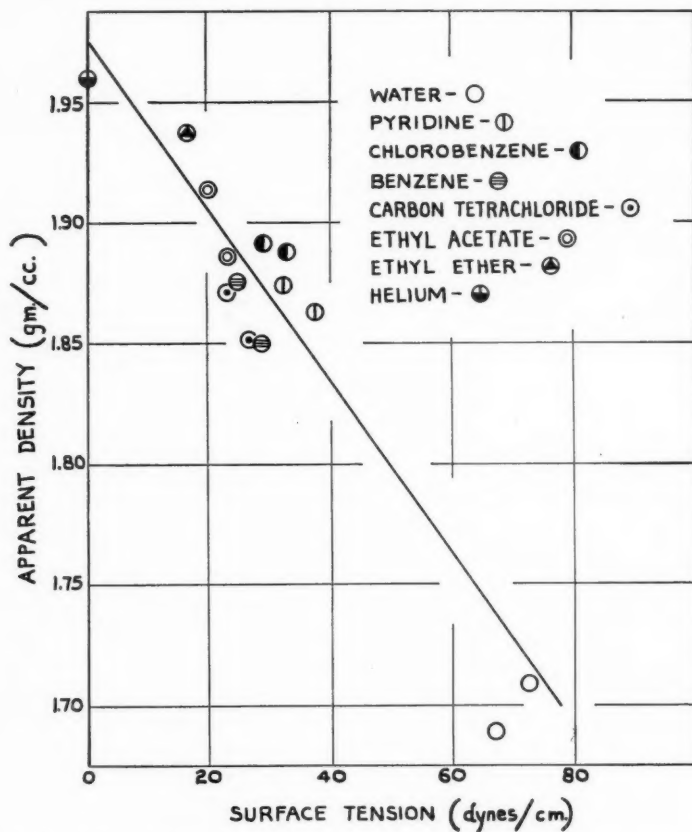| Sample No.	Carbon tetra-chloride	Ethylene glycol	Water	Chloro-benzene	Benzene	Pyridine	Ethyl acetate
A	1.38_2	1.81_5	1.82	1.79_9	1.82_6	1.88	1.91_7
B	1.43_2	1.82	1.84_6	1.83_2	1.84_8	1.91_9	1.89_7
C	1.59_8	1.83	1.85_9	1.89_3	1.91_4	1.93_5	1.96_5
D	1.69	1.89_2	1.86_2	1.92_2	1.97_5	1.97_4	1.98_8
E	1.82_2	1.92_7	1.86_2	1.93_9	1.96_9	2.01_3	2.01_2
F	1.92_5	1.92_6	1.86_3	1.96_9	2.00_2	2.01_8	2.02_9

FIG. 4. *Apparent density of charcoal sample C.W.S.N. 178 B-2 as function of the surface tension of the liquids.*

TABLE V

APPARENT DENSITIES OF PROGRESSIVELY ACTIVATED SAMPLES IN SEVERAL LIQUIDS AT 55° C.

S.B.T. No. 72   Density, gm./cc. $T = 55°$ C.

Sample No.	Carbon tetra-chloride	Ethylene glycol	Water	Chloro-benzene	Benzene	Pyridine	Ethyl acetate
A	1.38_3	1.81_4	1.81	1.82_3	1.84_7	1.90	1.93_5
B	1.43_4	1.81_8	1.83_6	1.85_4	1.86_7	1.92_8	1.91_5
C	1.60_4	1.82_9	1.84_5	1.91_7	1.93	1.94_3	1.98_2
D	1.69_3	1.88_8	1.84_2	1.94_7	1.99_4	1.98_3	2.00_3
E	1.83_5	1.92_5	1.84_8	1.96_4	1.99_1	2.02_3	2.03
F	1.93_9	1.92_6	1.84_6	1.99_4	2.02_2	2.03_1	2.04_9

the total pore volume filled for each sample by the various liquids are given for the two temperatures in Tables VI and VII. Finally, the necessary values of density in helium, density in mercury, surface area, and volume-to-area ratio are given for all samples in Table VIII, although some of these values have been reported earlier (11).

TABLE VI

FRACTION OF PORE VOLUME FILLED BY LIQUID AT 25° C. FOR SAMPLES OF TABLE IV

S.B.T. No. 72

Sample No.	Total pore volume, cc./gm.	Fraction filled by:						
		Carbon tetra-chloride	Ethylene glycol	Water	Chloro-benzene	Benzene	Pyridine	Ethyl acetate
A	0.41	0.69_7	0.91_7	0.91_9	0.91	0.92	0.95	0.97
B	0.42	0.71	0.90	0.91_5	0.91	0.91_7	0.95	—
C	0.49	0.79	0.90_5	0.92	0.93_5	0.94_5	0.95_6	0.97
D	0.54	0.83	0.93	0.91	0.94	0.97	0.97	0.97_6
E	0.56	0.89	0.94	0.90_8	0.94_5	0.96	0.98	0.98
F	0.65	0.93	0.93	0.90	0.95	0.96_6	0.97	0.98

Discussion

The data of Table II for sample S.B.T. No. 95, which are represented in Fig. 3, indicate that as a first approximation there exists a relation between surface tension of the liquid and the apparent density. It should be noted also that the value of the density at zero surface tension, obtained by extrapolating the line through the liquid density points, agrees closely with the density value determined by use of helium. In general also, density values obtained at the higher temperature, and thus at a lower surface tension of the same liquid, are higher than the values obtained at the lower temperature. Unfortunately, the variation in surface tension of the liquid due to tem-

TABLE VII

FRACTION OF PORE VOLUME FILLED BY LIQUID AT 55° C. FOR SAMPLES OF TABLE V

S.B.T. No. 72

Sample No.	Total pore volume, cc./gm.	Fraction filled by:						
		Carbon tetra-chloride	Ethylene glycol	Water	Chloro-benzene	Benzene	Pyridine	Ethyl acetate
A	0.41	0.69_7	0.91_8	0.91	0.92	0.93	0.96	0.97_6
B	0.42	0.71	0.90	0.91	0.92	0.92_5	0.95_5	0.95
C	0.49	0.79	0.90	0.91	0.94_6	0.95	0.96	0.97_7
D	0.54	0.83	0.92_6	0.90_5	0.95_5	0.96	0.97	0.98_5
E	0.56	0.89_5	0.94	0.90	0.95_7	0.97	0.98_5	0.99
F	0.65	0.936	0.93	0.89	0.96	0.96_7	0.98	0.99

TABLE VIII

DATA REQUIRED TO EVALUATE MEAN PORE RADIUS

Sample No.	Density in mercury, gm./cc.	Density in helium, gm./cc.	Area, sq. metres/gm.	Mean pore radius, Å
S.B.T. No. 72				
A	1.09_9	1.98	644	12.7
B	1.08_5	2.01_5	792	10.6
C	1.01_8	2.02	895	10.9
D	0.97_4	2.03_7	963	11.2
E	0.95_4	2.05	1070	10.5
F	0.89_1	2.07	1136	11.3
S.B.T. 95	0.89_9	2.18	1220	10.7
C.W.S.N. 178 B-2	0.53_5	1.96	1840	14.8

perature is not large, and the data should be extended over a wider temperature range.   Three liquids were the exceptions to this rule for all carbon samples studied.   These were glycerine, ethylene glycol, and water, and all gave lower apparent density values at the higher temperature.

Although the data for sample C.W.S.N. 178 B-2 are not nearly as extensive as for the cocoanut shell sample, again in general the lower surface tension liquids yield higher density values for the carbon.

In the case of the cocoanut shell series, S.B.T. No. 72, it is clear that some factor other than surface tension is involved in the apparent density value. For slightly activated carbons it is seen that carbon tetrachloride, for example, may give lower density values than water, although that result would not be expected from the data on S.B.T. No. 95.   From the tables showing the fraction of the total pore volume filled for the several liquids on this series of carbons, it is apparent that during activation some property of the carbon is being altered so that a variation in the proportion of the total volume filled is brought about.

From the standpoint of the penetration theory, the size of the internal voids might be considered as the determining factor. On this basis it would appear that the average void size must be increasing as activation proceeds. This suggestion is not supported by the independent evaluation of mean pore size made by means of the total volume and area measurements. From these latter data it appears that the mean pore radius is substantially constant throughout the series. (Sample A has a higher value which may be due to the inability of nitrogen to penetrate the pores, giving a low surface area value). Further, it should be noted that for water a slight decrease in the fraction of the volume filled occurs as the extent of activation is increased. These results suggest that some factor other than the average pore dimension is involved.

The theory that compressibility of the liquids accounts for density variations will not explain these observations. As the volume-to-area ratio is nearly constant, wide variations in the amount which the liquids are compressed is not to be expected, unless the nature of the surface is altered. From the values of E_1 for nitrogen, the energy of adsorption of the first layer, reported earlier (11), the nature of the surface appears unchanged and only the extent of surface appears to vary as activation is continued. Also, carbon tetrachloride or benzene would not be expected to show lower density values than are exhibited in water.

From the viewpoint outlined in the introduction, the apparent density value will depend upon the free energy change brought about on immersion in the liquids. The value of the energy change is seen to depend both upon the surface tension of the liquid–vapour interface and upon the wetting angle at the solid–liquid interface. Variations in the wetting angle for the series of increasing activity could conceivably cause the observed variations in apparent density. On this basis, however, the change in wetting angle with temperature must be negligible for all the liquids except glycerine, ethylene glycol, and water. Too little is known concerning the factors that govern the value of a wetting angle (2, 3, 17) to permit further discussion at the present. The anomalous behaviour of water should be stressed, however, in view of its peculiar adsorption isotherm on charcoal. From the results with glycerine and ethylene glycol, similarities to the adsorption isotherm of water might also be expected in the adsorption isotherms of these substances.

To recapitulate, it appears that the value of the apparent density of charcoal immersed in a given liquid will be determined primarily by the surface tension of the liquid and by the wetting angle of the solid–liquid interface. Factors such as molecular size in relation to diameter of the internal voids or the compressibility of the liquid employed do not appear to explain the results adequately.

Acknowledgment

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THE PORE STRUCTURE AND ADSORPTIVE PROPERTIES OF SOME ACTIVATED CHARCOALS

III. THE APPARENT DENSITY OF WATER ADSORBED ON ACTIVE CHARCOAL[1]

BY J. A. MORRISON[2] AND R. McINTOSH[3]

Abstract

The apparent density of water adsorbed on four different charcoals at 20° C. has been measured by a method of helium displacement. At low relative pressures the density is appreciably higher than that of liquid water, but falls rapidly to nearly the normal density as the amount adsorbed increases. A very sharp drop in density occurs close to saturation, and is attributed to the blocking of the very small porous spaces through the advent of capillary condensation in this region. It is suggested that the apparent high initial density is due to the size of the molecules of the measuring fluid rather than to the compression of the adsorbed film.

The apparent density of the adsorbed water on the desorption branch of the isotherm differs from that on the adsorption branch, which suggests that the mechanisms of adsorption and desorption differ. An attempt has been made to evaluate the constants V_m and C of the multimolecular adsorption theory from one of the adsorption isotherms.

Introduction

The greater part of information concerning adsorption processes has been derived from measurements of the adsorption isotherms and heats of adsorption of vapours on solids. All of the several theories of adsorption that have been proposed include postulations about the nature of the adsorbed film. Relatively few direct measurements of the properties of the adsorbate have been made. In what follows, the density of water adsorbed on charcoal has been determined by a method of helium displacement with a view to establishing the value of this property as a guide to the adsorption mechanism. On the basis of published data, none of the theories seems to describe water adsorption adequately.

The occurrence of limited hysteresis in the adsorption of water on charcoal has lead to speculation concerning the applicability of the capillary condensation theory. It has been shown (10) that, using the concept of Cohan (5) of adsorption in annular rings, it is possible to derive a value of the mean pore radius that is in fair agreement with that derived from the ratio of the pore volume to the surface area of the charcoal. On the basis of capillary condensation, the slope of the adsorption branch of the isotherm is attributed to a lack of homogeneity of pore sizes, and analyses of the distribution of pore sizes and number of pores have been attempted (13). However, the same distribution should be obtained from the desorption branch, provided

only that the mechanism of desorption is different, and that no error has been made in the hypothesis. In general, for water adsorption, this criterion does not appear to be met, the desorption branch indicating a nearly homogeneous adsorbent in terms of pore size (e.g., Fig. 4).

McBain, Porter, and Sessions (14) have shown that charcoal expands when water is adsorbed, just as it does when other vapours are adsorbed. For this reason, McBain has rejected the capillary condensation theory for water adsorption. If the adsorbed water exists under menisci it should be under tension and should not expand the charcoal.

The multimolecular adsorption theory (3) treats water adsorption as a special case of multilayer formation where initially E_1, the heat of adsorption of the first layer, is less than E_L, the heat of liquefaction of the vapour. It is possible with the help of the theory to obtain an isotherm equation that fits the experimental isotherm, but there appears to be a discrepancy in the surface area values derived from it (3). The theory predicts that at the saturation pressure the capillaries are not full, a prediction verified by experiment (10).

Of several papers describing the determination of the density of adsorbed films, two are of interest here. De Vries (7) has measured the density of carbon dioxide, and Danforth and De Vries (6) the density of carbon tetrachloride and of acetone adsorbed on charcoal. In the interpretation of the results, these authors appear to have neglected the effect of the structure of the adsorbent, and the effect of the molecular size of the displaced fluid. By using several samples of charcoal whose physical properties were determined by independent measurements, an attempt has been made in the present investigation to evaluate the magnitude of these effects. It appears that they are of considerable importance.

Experimental

The method employed was similar to that of Filby and Maass (9) using the technique of gas expansion. A schematic diagram of the essential parts of the apparatus is shown in Fig. 1. The charcoal sample was contained in the bulb D, which could be detached from the system for weighing. The expansions with helium were made from the standard volume C to the cell D. C and D were made approximately of the same volume so that the precision was optimal. This section of the apparatus was totally immersed in a water-bath controlled to $20° \pm 0.02°$ C., which eliminated the necessity of making temperature corrections on the expansions, and greatly improved the reproducibility of the results. Pressures were read on a constant volume mercury manometer with glass scale attached to a manifold. Connection between the manifold and the part of the apparatus in the water-bath was made through the short manometer E. For each pressure measurement, the level of the mercury in one arm of the short manometer was brought to the tip of a fixed glass pointer. All pressures were corrected to a reference of a

mercury column at 0° C.   Ground glass check valves at the top of both arms of the short manometer made it possible to evacuate either side without drawing mercury into the system.

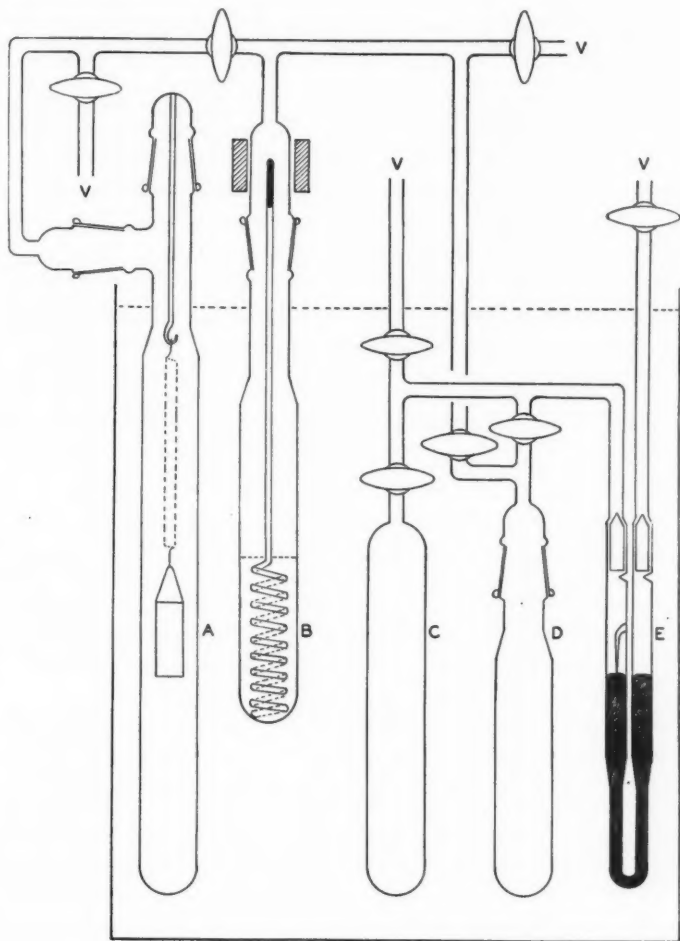
FIG. 1.   *Schematic diagram of the principal parts of the apparatus.*

Connections with the manifold and vacuum system were made at V shown in Fig. 1.   The charcoal was degassed by heating to approximately 130° C. and evacuating until a pressure of 5×10^{-5} mm. of mercury was maintained. Evacuation was performed with a two stage mercury diffusion pump, backed by a Hyvac oil pump.

To the manifold was attached the helium purification and storage system. The helium was purified by passing it slowly over degassed charcoal cooled in liquid air, and was stored in a 12 litre bulb. Just before use, it was passed again through the purification train. Any desired pressure within the system could be established with a Toepler pump. The pump was also of use in obtaining fine adjustment of the pressure in the manifold to balance that in the expansion system.

Different pressures of water vapour were developed by using solutions of sulphuric acid and water contained in *B*. The solutions were degassed thoroughly by freezing at dry ice temperatures and evacuating several times.

While water vapour was being adsorbed on the charcoal, the solution was agitated with a glass stirrer. The stirrer had a piece of soft iron sealed into the top, and was actuated by a solenoid on the outside.

A spring balance *A*, of No. 32 gauge phosphor-bronze wire, with an extension of approximately 2.7 cm./gm., was connected with the water reservoir *B* and the charcoal cell *D*, and was used to determine when the charcoal was in equilibrium with the water vapour. Approximately one gram of charcoal was contained in a basket made of copper screen, which was hung at the lower end of the spiral. The extension of the spiral was followed with a cathetometer.

Operation

After the charcoal had been degassed, the free volume in the cell *D* was determined by expanding helium from the calibrated volume *C* into *D*. The final pressure was followed for approximately eighteen hours. Slight drifts in pressure were sometimes observed immediately after the expansion, but these were attributed to the establishment of temperature equilibrium. No drifts extending over a period of hours such as reported by Howard and Hulett (12) were ever observed.

At least 48 hr. was allowed for the charcoal to come to equilibrium with the water vapour from *B*, and the free volume in the cell *D* was again determined. However, in this case the expansion was performed with a mixture of water vapour and helium. Before the expansion, *C* was filled with water vapour at the same pressure as in *D*, and an appropriate amount of helium was added quickly. When the pressure had become constant, the gas was expanded into *D*, and 18 to 24 hr. was allowed for equilibrium to be established. The free volume was calculated on the basis of the partial pressure of helium, which was obtained by subtracting the partial pressure of water vapour from the total pressure. That this procedure is permissible was shown by the determination of the volume of a glass bulb by expansion with several mixtures of helium and water vapour. Volumes so determined agreed within 0.05% with the volume as found by expanding dry helium. The volume of water adsorbed on the charcoal was determined then by the difference between the initial and final free volumes. The weight of water was found by detaching *D* from the apparatus and weighing. In this operation the pressure of helium

in D was brought up to atmospheric and the cell was stoppered firmly as soon as it was detached.   Altogether, a period of from seven to nine days was required for a single determination.

It is difficult to assign a value for the accuracy of the determinations owing to the possibility that the adsorbed film may not build up in the same manner in successive determinations.   On the basis of the results, it appears that the precision of the measurements is about 1% at saturation and about 3% at the lowest pressures used.   Unless the solubility of helium in the adsorbed film is considerably greater than in liquid water, no appreciable error is introduced by neglecting this factor.   Expansion of the charcoal particles when water is adsorbed (14) is also insufficient in magnitude to introduce errors.

Charcoals

In Table I are given data that describe some properties of the charcoals that were used.   Charcoal D was prepared by leaching charcoal C for 24 hr. with 50% aqueous hydrofluoric acid.   The charcoal was then washed thoroughly with distilled water and dried.   The densities of the charcoals in

TABLE I

A SUMMARY OF THE KNOWN PROPERTIES AND PREPARATIONS OF THE CHARCOAL SAMPLES

Charcoal	A	B	C	D
Manufacturer	National Carbon	Standard Barneby	National Carbon	National Carbon
Designation	*CWSN 178B-2*	Charge 72	*CWSN 212A–1X*	*CWSN 212A–1X*
Starting material	Wood	Cocoanut shell	Wood	Wood
Activation	Zinc chloride	Steam	Zinc chloride	Zinc chloride
Density in helium	1.91	2.07	2.11	2.09
Density in water	1.74	1.86	1.86	1.83
Density in mercury	0.54	0.89	0.66	—
Ash content, %	1.6	0.5	4.0	0.7
Surface area, m.²/gm.	1840	1140	—	—

helium, in water, and in mercury were measured at 20° C.   The densities in water were determined by Major J. C. Arnell of the Chemical Warfare Laboratories, Ottawa.   The surface areas were measured by nitrogen adsorption at −183° C. after the method of Brunauer, Emmett, and Teller (4).

Results

The results of the measurements of the density of water adsorbed on the four charcoals are recorded in Tables II to VI, and are plotted in Figs. 2 and 3. To bring the curves to the same relative basis, the apparent density is plotted against the percentage of the adsorption at saturation for each charcoal. Data in Tables II to V pertain to measurements on the adsorption branch of the isotherms, while those in Table VI refer to measurements on the desorption branch for charcoal D.

It is at once apparent that the plots in Figs. 2 and 3 are of similar form, characterized by high density at small amounts adsorbed, followed by a rapid

TABLE II

DATA REQUIRED FOR THE APPARENT DENSITY OF WATER ADSORBED ON CHARCOAL A
(33.27 GM.)

Run No.	Time to eq. with water vapour, hr.	p/p_0	Final free vol. of cell, cc.	Adsorbed water			x/m	x/x_s, %
				Volume, cc.	Weight, gm.	Apparent density		
2	48	1.00	171.27	32.65	31.16	0.95_4	0.937	100
3	101	0.74	185.55	18.37	18.86	1.02_7	0.567	60.3
4	120	0.74	183.42	20.50	20.78	1.01_4	0.625	66.4
5	81	0.59	199.48	4.44	5.18	1.16_6	0.156	16.6
6	56	0.59	199.74	4.18	4.86	1.16_2	0.146	15.6
7	51	0.67	194.22	9.70	9.89	1.02_0	0.297	31.6
8	80	0.66	194.69	9.23	9.70	1.05_1	0.292	31.1
9	80	0.87	175.13	28.79	29.41	1.02_1	0.884	94.2
10	77	0.91	174.39	29.53	30.04	1.01_7	0.903	96.0
11	72	0.97	173.27	30.65	31.01	1.01_2	0.932	99.3
13	109	1.00	171.30	32.62	31.35	0.96_1	0.942	100
14	78	0.72	190.49	13.43	13.81	1.02_8	0.415	44.2
15	55	0.62	198.24	5.68	6.57	1.15_7	0.198	21.1

TABLE III

DATA REQUIRED FOR THE APPARENT DENSITY OF WATER ADSORBED ON CHARCOAL B
(38.66 GM.)

Run No.	Time to eq. with water vapour, hr.	p/p_0	Final free vol. of cell, cc.	Adsorbed water			x/m	x/x_s, %
				Volume, cc.	Weight, gm.	Apparent density		
1	54	1.00	186.62	16.23	14.35	0.88_4	0.371	100
2	68	0.77	190.36	12.49	11.81	0.94_6	0.306	82.5
3	53	0.58	195.10	7.75	7.50	0.96_3	0.194	52.2
5	49	0.47	199.51	3.34	3.48	1.04_2	0.090	25.2
6	72	0.53	196.85	6.00	5.76	0.96_0	0.149	40.2

decrease as the amount adsorbed increases, and finally an abrupt drop in density very close to saturation. While more experimental points would be desirable to define the curves quantitatively, this was not thought necessary to the scope of this paper. In addition the very lengthy period required to accumulate the data had to be considered. However, there appear to be sufficient points to establish the form of the curves with reasonable certainty.

The apparent high density that is observed at low relative pressures is generally attributed to compression of the adsorbate on the active part of the surface (2, p. 420). That the high density results from combination of the water with constituents of the ash is excluded by the determinations on charcoal D. Charcoal D was prepared from charcoal C by leaching out a large portion of the ash, yet reference to Fig. 3 shows that this has not reduced

TABLE IV

DATA REQUIRED FOR THE APPARENT DENSITY OF WATER ADSORBED ON CHARCOAL C
(34.54 GM.)

Run No.	Time to eq. with water vapour, hr.	p/p_0	Final free vol. of cell, cc.	Adsorbed water			x/m	x/x_s, %
				Volume, cc.	Weight, gm.	Apparent density		
1	48	1.00	181.30	23.04	21.62	0.93_9	0.626	100
3	54	0.70	196.30	8.04	8.93	1.11_0	0.259	41.4
4	53	0.72	193.42	10.92	10.85	0.99_4	0.314	50.1
5	49	0.65	198.83	5.51	6.33	1.14_9	0.183	29.2
6	52	0.72	193.44	10.90	10.95	1.00_5	0.317	50.6
7	54	0.74	191.51	12.83	12.80	0.99_8	0.371	59.2
9	54	0.90	182.85	21.49	21.18	0.98_6	0.613	97.9
10	51	0.83	185.60	18.74	18.37	0.98_1	0.532	85.0

TABLE V

DATA REQUIRED FOR THE APPARENT DENSITY OF WATER ADSORBED ON CHARCOAL D
(33.33 GM.)

Run No.	Time to eq. with water vapour, hr.	p/p_0	Final free vol. of cell, cc.	Adsorbed water			x/m	x/x_s, %
				Volume, cc.	Weight, gm.	Apparent density		
1	51	0.82	188.86	15.89	15.97	1.00_5	0.479	74.5
2	55	0.76	193.63	11.12	12.44	1.11_9	0.373	58.0
4	53	0.76	193.48	11.27	12.20	1.08_2	0.366	56.9
5	54	0.70	197.87	6.88	8.05	1.17_0	0.242	37.5
6	52	0.78	191.99	12.76	13.32	1.04_3	0.400	62.2
8	65	0.94	183.08	21.67	21.15	0.97_6	0.634	98.7
9	52	1.00	181.73	23.02	21.42	0.93_2	0.643	100

TABLE VI

DATA REQUIRED FOR THE APPARENT DENSITY OF WATER ADSORBED ON CHARCOAL D
(33.33 GM.)—DESORPTION BRANCH OF THE ISOTHERM

Run No.	Desorption time, hr.	Final p/p_0	Final free vol. of cell, cc.	Adsorbed water			x/m	x/x_s, %
				Volume, cc.	Weight, gm.	Apparent density		
1	76	0.53	184.13	20.62	19.52	0.94_6	0.586	91.2
2	75	0.50	191.07	13.68	13.40	0.98_0	0.402	62.5
3	74	0.43	202.09	2.66	2.84	1.06_8	0.085	13.2
4	74	0.47	197.33	7.42	7.32	0.98_7	0.220	34.2
5	74	0.49	190.58	14.17	13.35	0.94_2	0.401	62.4
6	74	0.49	190.50	14.25	13.25	0.93_0	0.398	61.9

Runs 1 to 5—desorption from saturation.
Run 6—desorption from $p/p_0 = 0.85$.

the apparent density of the water. Also, Danforth and De Vries (6) report high initial densities for carbon tetrachloride and for acetone on charcoal, substances that would not be expected to form complexes analogous to hydrates with the constituents of ash.
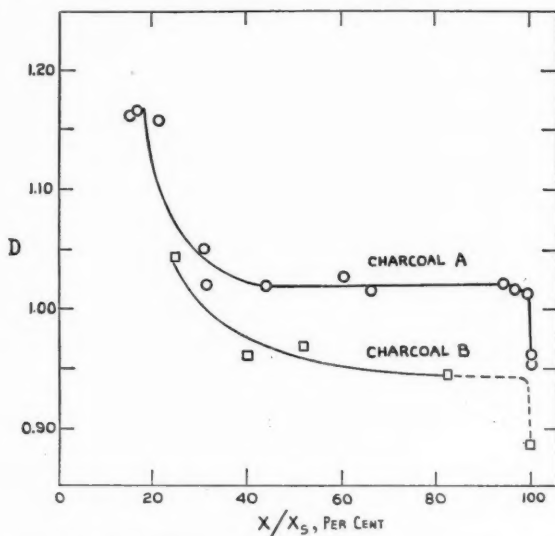

FIG. 2.   *Plot of the apparent density of adsorbed water, D, versus the per cent of adsorption at saturation, x/x_s %, for charcoals A and B.*

Because the energy change in adsorption, particularly with water adsorbed on charcoal, is relatively small, it is difficult to visualize the adsorbate subjected to large compressional forces. Too, the work of Bangham and coworkers (1) suggests that the adsorbed film is mobile; this would not be expected if it were under high compression. Another explanation, which has not been advanced, is that the apparent high densities arise from the method of measurement. At low relative pressures, it may be presumed that the adsorbate exists as isolated molecules or as small groups of molecules. Under such circumstances, it seems reasonable to expect that the small helium atoms, making up the displaced fluid, may measure more closely the true volume of the water molecules, as distinct from the volume occupied by the water molecules in the liquid state.

There appears to be sufficient experimental evidence to establish the very sudden decrease in the density of the adsorbed water at saturation. With charcoal *B* a mishap, in which the water from the thermostat came in contact with the charcoal, prevented further measurements. However, in view of the results with the other three charcoals, it seems permissible to indicate the drop in density by the dotted portion of the curve in Fig. 2. For an explanation of the sudden decrease in density, it is necessary to make reference

to the work of McIntosh *et al.* (10, 11), where it was shown that even when charcoal is immersed in liquid water, a part of the structure is not accessible to the water molecule. This small volume, as determined from the apparent densities of the charcoal in water and in helium, amounts to 0.05 to 0.07
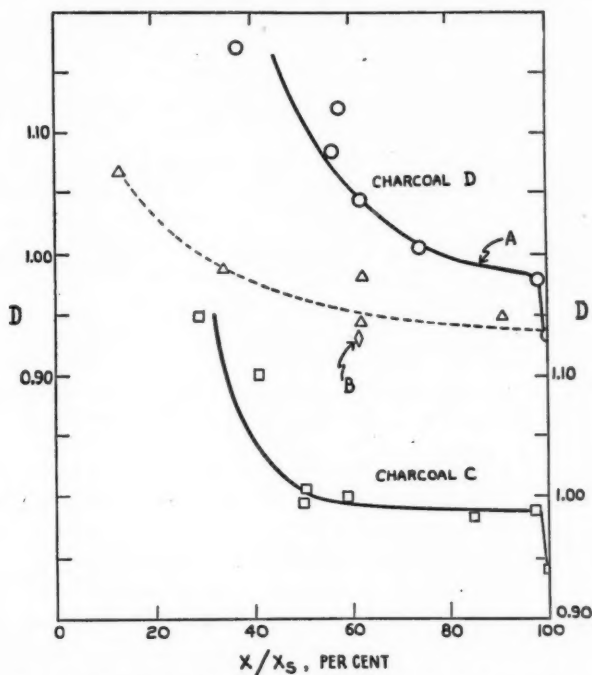

FIG. 3. *Plot of the apparent density of adsorbed water, D, versus the per cent of adsorption at saturation, x/x, %, for charcoals C and D. The dotted curve represents desorption.*

cc. per gm. for the four charcoals studied here. Calculation shows that, if the measured volume of the water at saturation is corrected by such an amount, the sharp drop in the density is practically eliminated*. Perfect agreement would not be expected from such a calculation because there is not a means of determining whether all the very small porous spaces, which are blocked when the charcoal is immersed in liquid water, are blocked when the charcoal is exposed to water vapour at the saturation pressure.

Although the density curves in Figs. 2 and 3 representing adsorption are of similar form, it will be noted that the value of the density just before the drop at saturation is different in each case, ranging from 0.94 for charcoal *B*

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* *In a previous publication (10) it was assumed that the submicro pores became blocked to nitrogen at a relative pressure of 0.87. The validity of that assumption is doubtful in view of the present findings with helium. However, as the measurements in the case of nitrogen were made at −183° C., and with helium at +20° C., it is possible that the blocking of the submicro pores may have occurred at the lower moisture content of the carbon in the experiments with nitrogen.*

to 1.02 for charcoal A, a somewhat larger variation than might be expected. However, this may be accounted for, if the adsorbed film has a different arrangement on each charcoal. Reference to the data in Table I shows that the volume of porous space, as determined from the densities of the charcoals in helium and in mercury, is larger for charcoal A than for charcoal B, by a factor of 2.1, while the surface area of charcoal A exceeds that of charcoal B by a factor of 1.6. This suggests that the average size of the porous spaces is greater for charcoal A, and geometric restrictions on the number of adsorbed layers built up would be expected to be less than for charcoal B. With charcoals C and D, where presumably the distribution of sizes of the porous spaces is very similar, the densities of the adsorbed water before the drop at saturation are 0.99 and 0.98, respectively. The nature of the surface may be a factor also, but its effect cannot be determined from these experiments.

The curve of the density of the adsorbed water during desorption, shown in Fig. 3, suggests that there is a distinct difference between the adsorption and desorption mechanisms. The points from which the curve was drawn were obtained by desorbing from saturation. If the sudden drop in density at saturation on the adsorption branch is due to blocking of the very small porous spaces, it appears that the blocking persists during desorption. That the effect is not limited to the desorption from saturation is shown by the last determination in Table VI. The water was adsorbed on the charcoal at a relative pressure of 0.85, and the density of the adsorbed water should have been that indicated by point A in Fig. 3. The water was then desorbed to a relative pressure of 0.49, and the determined density is indicated by point B, which lies on the desorption curve within experimental error.

It is generally believed that the occurrence of limited hysteresis is an indication of capillary condensation. However, if both the adsorption and desorption processes are governed by a condensation mechanism, the difference in density between the adsorbed water on adsorption and on desorption should not exist. In addition, both branches of the isotherm should have similar slopes. That this is not so is shown by the plot for charcoal D in Fig. 4. The only view consistent with experiment seems to be that the adsorption of water takes place on the entire surface of the charcoal, with capillary condensation occurring only very close to the saturation pressure, as indicated by the blocking of the very small porous spaces. Desorption may then occur from menisci in the capillary spaces, the process being governed by the mechanism of condensation.

Brunauer, Deming, Deming, and Teller (3) have sought to include the special case of water adsorption on charcoal within the general multimolecular adsorption theory. To test the applicability of the theory, the adsorption of water on charcoal A at low relative pressures was measured. The data are given in Table VII, and the complete isotherm is plotted in Fig. 5. Following the suggestions of Brunauer *et al.* (3), a plot of the data was made in the form $\dfrac{p}{v(p_0-p)}$ versus p/p_0, in order to evaluate the constants V_m

and C of the isotherm equation.   The resulting plot was linear only up to a relative pressure of 0.15.   From this linear portion, a value of V_m of approximately 100 cc. at S.T.P. and of C of approximately 3.2 was derived.   To be consistent with the theory and with the surface area as determined by nitrogen
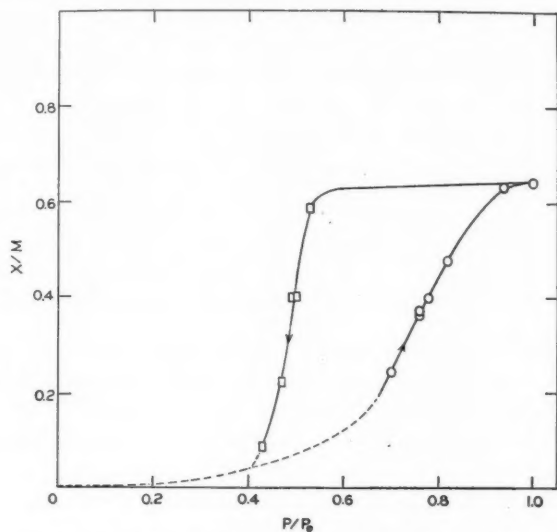

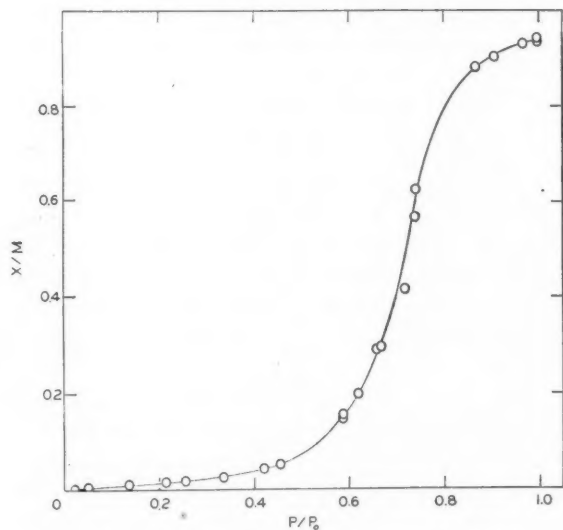FIG. 4.   *The adsorption isotherm of water on charcoal D.*

FIG. 5.   *The adsorption isotherm of water on charcoal A.*

TABLE VII

ADSORPTION DATA AT LOW RELATIVE HUMIDITIES FOR CHARCOAL A

p/p_0	x/m, gm./gm.			
	1	2	3	Average
0.023	0.0039	0.0041	0.0039	0.0040
0.051	0.0062	(0.0071)	0.0063	0.0064
0.137	0.0102	0.0102	0.0100	0.0101
0.257	0.0178	0.0179	0.0175	0.0178
0.337	0.0264	0.0263	0.0261	0.0263
0.422	0.0416	0.0410	0.0410	0.0412
0.217	0.0148	0.0146	0.0150	0.0148
0.456	0.0513	0.0511	0.0511	0.0512

adsorption, V_m should have a value of approximately 700 cc. at S.T.P. and C should be less than unity. Emmett (8) has suggested that, since the BET plots are very sensitive to slight variations in C, the reason for the discrepancy may lie in the change in C as the surface is partially covered with water vapour.

Although it is not possible to establish conclusively the mechanism of water adsorption from existing information, it appears worth while to summarize the experimental evidence. The existence of limited hysteresis is the principal point suggesting capillary condensation. The fair agreement between the values of the mean pore radius calculated by either the Cohan formula (5) for adsorption or the Kelvin equation for desorption with that determined from the ratio of the total internal volume to the total surface area supports this view. However, the expansion of the charcoal when water vapour is adsorbed (14) suggests that the mechanism of adsorption does not differ markedly from that by which other vapours are adsorbed. The marked difference in density of the adsorbed phase established during adsorption from that established during desorption is most easily explained by assuming the formation of menisci at saturation or on desorption. Also, the high values of the density of the water adsorbed at low relative pressures suggest that the formation of a non-continuous film is the first step in the adsorption process.

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THE INFLUENCE OF MEMBRANE PREPARATION ON THE OSMOTIC PRESSURE OF POLYVINYL ACETATE IN ACETONE[1]

By R. E. Robertson[2], R. McIntosh[3], and W. E. Grummitt[4]

Abstract

A full account of the experimental procedures used to determine the number average molecular weights of a series of polyvinyl acetates is given. Adsorption of polyvinyl acetate on a cellophane membrane is demonstrated. The importance of this phenomenon is increased when cells of large ratio of membrane surface to cell volume are used. The presence of small amounts of sodium hydroxide in the membrane eliminates detectable adsorption and alters the osmotic pressure values. This change does not appear to be due to imperfect semipermeability of the membranes, and no adequate explanation of the phenomenon has been as yet discovered.

In the past several years the publications of Flory and Huggins, Mark and others* have developed considerably the theoretical aspects of the behaviour of macromolecules in solution. At the same time improvements in the design of osmotic cells have decreased the difficulty of such determinations (9, 10, 19) until the evaluation of the number average molecular weight of macromolecules appears straightforward. However, a good deal remains unknown concerning the mechanism by which the semipermeable membrane functions (see, for example, Fuoss and Mead (10)) and the choice and preparation of such membranes still appears arbitrary. Some authors, notably Carter and Record (7), have found cellophane membranes satisfactory, while others have remarked that such membranes were found unsuitable (19) but have not stated wherein the difficulty lay. At the same time such factors as the time lags involved in the establishment of equilibrium pressures have not been adequately explained.

In an attempt to demonstrate that changes of viscosity of solutions of polymers could be attributed to molecular weight changes (see another paper in this series), an osmometer was constructed similar to others that have already been described. It became evident immediately that factors of importance from the experimental viewpoint had not been adequately assessed in other publications, or were not operative under slightly different experimental conditions. These factors made necessary an extensive investigation into the preparation of cellophane membranes and the influence of that preparation on the results obtained. Since a complete explanation of certain results has not been possible, a very full description of the experimental methods and findings is given below.

The results were obtained on polyvinyl acetate dissolved in acetone, but certain evidence exists that similar phenomena may be found with other polymer–solvent systems. To sum up the conclusions reached in studying the polyvinyl-acetate–acetone system, it appears that:

1. Adsorption of polymer occurs on the cellophane membranes when the membranes are prepared by the Carter and Record method.

2. The amount of adsorption is sufficient in cells of large ratio of membrane surface to cell volume to cause large errors in the molecular weight values that are obtained.

3. Time lags in the establishment of equilibrium osmotic pressures are caused mainly by the adsorption process.

4. Adsorption may be decreased to inappreciable amounts by treating the cellophane membranes in caustic solution before accommodation to the organic solvent, provided that treatment subsequent to the caustic wash does not remove all the alkali from the membrane. The amount that must be retained on the membrane is not known exactly, but relatively wide variation of the washing treatment does not appear to alter the membrane behaviour appreciably.

5. Molecular weight values may be obtained with membranes prepared by the Carter and Record method by permitting adsorption to occur and then refilling the cell several times with fresh solution of the same concentration.

6. The molecular weights obtained as described in 5 do not correspond with those obtained using caustic treated membranes, and the results cannot be explained by a difference in permeability of the membranes to small molecular weight material.

Since these points require careful substantiation, and since it is necessary to show that the results do not depend upon the heterogeneity of the polymer samples in an obvious manner, a full account of the experimental equipment and procedures follows.

Experimental

Polymers

Commercial samples of polyvinyl acetate were used throughout the investigation. No attempt was made to prepare homogeneous materials. Insoluble polymer was removed from the samples by dissolving them in acetone and filtering carefully. After filtration the polymer was precipitated from the acetone solution (5% by weight) by pouring it slowly into water. The water was stirred and the polymer collected around the stirrer, from which it was removed periodically. The precipitated polymer was partially dried by prolonged evacuation at room temperature. When in this partially dried state it was cut into small pieces and then dried thoroughly by vigorous evacuation and stored over Drierite. One large sample of each grade of polymer was prepared in this way and the same preparation was used throughout the investigation.

A'cetone

Both reagent grade and c.p. acetone, which was stored over Drierite, were used.   No variation in behaviour between different batches of acetone was ever observed.

Osmometer

A dynamic type of osmometer similar in design to that of Van Campen (6) and Montonna and Jilk (19) was used (Fig. 1).   The operation of such an
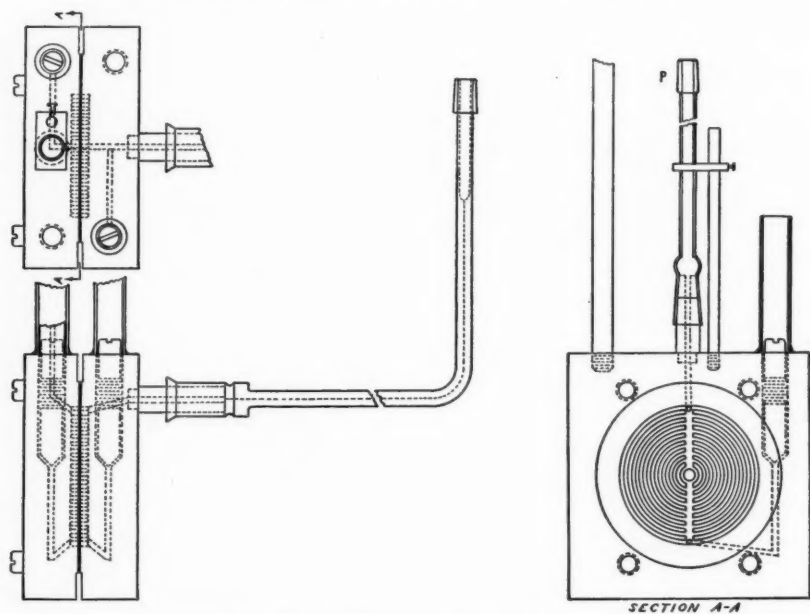
FIG. 1.   *Dynamic osmotic cell.*

osmometer using a counter pressure manometer has been fully described by Carter and Record (7).   In dealing with heterogeneous samples, this type of osmometer offers certain advantages.   Chief of these is the use of relatively high concentrations of polymer; this enables one to ensure that the membrane is semipermeable.   A second advantage is that the relative permeability of the membrane to solvent is given directly by the slope of the line representing rate of movement of the meniscus as a function of pressure.   This measurement was essential in establishing the characteristics of the membrane before and during its use with solutions.

The disadvantages of this type of cell were the tediousness of making measurements, the very precise temperature control required (temperature fluctuations of $0.001°$ C. are easily detected by variations in the rate of

meniscus movement) and the relatively long extrapolation of the π/C versus C plots to zero concentration.

In common with the cell recently described by Fuoss and Mead (10) and that used by Flory (9), the ratio of membrane area to cell volume is large. It is this fact that led to the discovery of the adsorption effects, and a large value of the ratio of area to volume is therefore a serious disadvantage of these cells if adsorption occurs on other types of membranes and with other polymer–solvent systems. A table of estimated values of the area–volume ratio for several cells is given in Table I.

TABLE I

AREA–VOLUME RATIO OF OSMOMETERS

Osmometer	Membrane surface/cell volume, cm.$^{-1}$
Van Campen cell (6)	20
Meyer, Wolff and Boissonnas (18)	2.0
Fuoss and Mead (10)	5.0
Carter and Record (7)	1.6
Flory (9)	3.1
Cell used in this investigation	4.5

Thermostat Control System

The required temperature control was obtained with the following arrangement. A large metal bath containing 10 gal. of transformer oil was completely enclosed in an air-bath maintained at about 29° C. In the oil-bath proper was placed a Wheatstone bridge, two arms of which were manganin and two iron. A galvanometer (0.0049 μamp. per mm.) was connected across the bridge, the other ends of which were connected with a 6 v. storage battery. The resistances of the arms (about 450 Ω) were adjusted roughly to bring the bridge to balance at 30° C. Final adjustment of resistance was made on a thermostatically controlled Leeds and Northrup resistance box in series with one of the manganin arms. An electric heater of about 3 w. capacity was employed in the oil-bath, and was controlled by a photoelectric relay actuated by the light spot from the galvanometer. The heating period of the bath was interrupted by a shutter operating in front of the photoelectric cells, as suggested by Eichelburger (8). Calculation of the thermostat temperature variations from a knowledge of the heating period, the heater input, and the thermal capacity of the bath showed a control of 8/10,000° C. This calculation was found to check with experiment, which showed a maximum deviation of 7/10,000° C. The performance of the thermostat was extremely reliable; this was partly due to very good stirring.

Membranes

Two types of membrane were employed, designated hereafter as Carter and Record membranes and as caustic treated membranes, respectively.

Both these types were prepared from No. 600 P.T. Cellophane (not water-proofed) supplied by Canadian Industries Ltd.

To prepare the C and R^* membranes the cellophane was first washed several times with warm water to remove plasticizers. The permeability of the membrane to solvent was then established by soaking in ethyl-alcohol–water solutions. Low permeabilities were obtained by soaking in solutions of high alcohol content, and high permeabilities by soaking in solutions of high water content exactly as described by Carter and Record. Before transfer to anhydrous acetone the membranes were stored in anhydrous ethanol for a given period. Too long storage in anhydrous ethanol reduced the permeability, and a fixed period for this stage of the preparation (12 hr.) was used. No change in permeability with time occurred on storage in anhydrous acetone.

The preparation of caustic treated membranes was somewhat similar. The membrane was first soaked in warm water and then in a solution of known concentration of caustic for a given time at room temperature. The permeability to solvent was established at this step as shown in Table II. The influence of the time of soaking in the caustic solution on the permeability was not examined thoroughly, but appears to be of lesser importance than the concentration. Excess caustic was then removed by dipping either in water or 50 : 50 ethanol–water. The membranes were then stored for 15 min. in anhydrous ethanol, and finally transferred to anhydrous acetone.

TABLE II

PERMEABILITY OF CAUSTIC TREATED CELLOPHANE TO ACETONE AT 30° C.**

NaOH, %	Time at 25° C., min.	d, cm. $\times 10^3$†	$P \times 10^{13}$‡
2	15	7.5	9.0
4	15	9.0	12.0
6	15	(14.6)	16.4
8	15	14.0	21.0
10	30	10.0	36.0

** *Canadian Industries Ltd.   Cellophane No. 600 P.T.*
† *Thickness of membrane.*
‡ *P = specific permeability defined by Manegold and co-workers (3, 16) by the equation P = Dηd.*
  D = cc./cm.²/sec. for a pressure of 1 dyne/cm.².
  η = viscosity of the solvent in poises.

The presence of caustic in the membranes was established by burning off the cellophane and testing the water extract of the ash. Whenever all the caustic had been removed from the membrane, its behaviour was similar to that of a C and R membrane, except that its permeability to solvent was greater and it was no longer semipermeable to low molecular weight polymer.

*Carter and Record, Ref. (7).

So long as caustic was left in the membrane, its behaviour was different from that of a C and R membrane. The semipermeability of the membrane persisted at values of solvent permeability nearly 50 times greater than a semipermeable C and R membrane. Thus, with a C and R membrane the small molecular weight material could be detected in the solvent half-cell when a sample of Gelva 15 was used if the specific permeability exceeded a value of 0.35×10^{-13}. With a caustic treated membrane no polymer from a similar solution could be detected when the permeability was 16.4×10^{-13}. Obviously, in using higher molecular weight grades, semipermeability was more easily obtained with both types of membrane. For Gelva 360, a fully swollen C and R membrane could be used, but, for Gelva 45, membranes of lower solvent permeability were required. Properly prepared, caustic membranes (up to 6% sodium hydroxide for 15 min.) were found to be semipermeable to all types of polymer grade studied. Two tests for semipermeability were employed. In the first, the contents of the solvent half-cell was pipetted into an aluminium weighing bottle of known weight, and the thimble and contents quickly weighed. The sample was then evaporated to dryness and the container again weighed. Blank determinations permitted correction for any corrosion of the brass osmometer cell.

The second test was found to be somewhat more sensitive and more convenient. In this case the contents of the solvent half-cell was run into a small beaker of water. The appearance of turbidity indicated that polymer was present. Quantitative tests with this procedure showed that a solution of 0.01% concentration by weight could be detected with certainty and of 0.005% concentration by weight gave a very faint cloud. Since in testing any membrane for semipermeability a solution of 3% by weight was placed in the solution half-cell, a membrane designated as semipermeable allows less than 0.2% of the concentration in the solution side to diffuse through the membrane.

Equilibrium Osmotic Pressures

The time to constant osmotic pressure was established for both C and R and caustic treated membranes. The time to final pressure was between six and eight hours for the C and R membranes, in agreement with that reported by other investigators, and about one-half hour, or almost exactly the time for thermal equilibrium to be established, for the caustic treated membranes. No downward drift with time was ever observed with either type of membrane, although values were taken for as long as 72 hr. in some cases. From the criteria of semipermeability of the membranes and the constancy of osmotic pressure with time, values obtained with either type of membrane should be true osmotic values.

Intrinsic Viscosities

Intrinsic viscosities were measured in the ordinary manner by means of an Ostwald type viscometer. A kinetic energy correction was applied, and amounted to about 6% in the worst case.

Preparation and Handling of Solutions

All solutions were made up by weight and recalculated in terms of grams per 100 cc. of solution, from a knowledge of the density of pure acetone at the temperature of the measurement. Both in the case of viscosity and osmotic determinations the densities of the solutions were assumed to be the same as that of pure acetone.

In filling the viscometer and the osmometer at least four rinses were always employed, and this number was found to be sufficient. In handling the solutions, transfer was made by blowing the liquid into the receptacle by dried filtered air.

Results

Adsorption Effects on Carter and Record Type Membranes

Osmotic pressure measurements made with C and R membranes gave fair rectilinear plots of π/C versus C for Gelvas 360, 150, 45, and 15. Contrary, however, to the predictions of relative molecular weights from intrinsic viscosity measurements (see Table VIII), grades 150, 45, and 15 gave π/C values that were equal to or lower than corresponding values for 360. The results given in Table III were all equilibrium values and no polymer was

TABLE III

OSMOTIC DETERMINATIONS WITH CARTER-RECORD MEMBRANES

Conc., gm./ 100cc.	μ^*	π, gm./ cm.^{2}	π/C	Remarks	Conc., gm./ 100cc.	μ^*	π, gm./ cm.^{2}	π/C	Remarks
		Gelva 360					Gelva 150		
2.88	0.46	15.40	5.35		1.31	0.58	4.52	3.45	
1.95	0.46	9.12	4.67		2.84$_5$	0.50	19.60	6.90	
5.61	0.21	70.60	12.60		4.24	0.22	41.80	9.88	
3.86	0.29	34.00	8.60	$(\pi/C)_{c=0}$	1.40	0.23	5.02	3.58	$(\pi/C)_{c=0}$
3.95	0.26	36.40	9.22	$=0.62$	3.17	0.25	16.48	5.20	$=0.65$
2.57	0.57	15.25	5.94		3.31	0.25	25.45	7.70	
1.28	0.62	4.40	3.44		1.76	0.23	7.97	4.50	
3.47	0.44	27.60	7.96		1.91$_5$	0.50	8.60	4.49	
		Gelva 45					Gelva 15		
1.69	0.22	6.52	3.65		1.60	0.22	5.55	3.47	Low
3.05	0.21	21.21	7.07	$(\pi/C)_{c=0}$	2.38	0.18	18.20	7.65	
				$=0.285$			17.70	7.44	
4.12	0.20	37.20	9.05		1.97	0.18	13.35	6.77	
					1.25	0.19	4.58	3.65	$(\pi/C)_{c=0}$
					0.79	—	2.19	2.77	$=0.40$
					3.11	0.16	35.20	11.30	
					1.59	0.24	10.72	6.74	

* *These values represent the permeability of the membrane to solvent determined with solution in one half-cell, and are not corrected for membrane thickness, and have obviously not been converted into the units of specific permeability.*

detected in the solvent half-cell.   The results were also reproducible provided that the same experimental procedures were followed.   In all instances there was a long time lag of between six and eight hours while the osmotic pressure built up to its equilibrium value.   Similar time lags had been noted by Flory (9), Gee (11), Gee and Treloar (12), and Carter and Record (7).

An attempt to determine the cause of these anomalous results was made by washing out the solution half-cell with more solution of the same concentration after the first equilibrium value had been attained.   This treatment brought to light two phenomena.   First, the time to equilibrium pressure was sharply reduced, in the case of low permeability membranes, to a period of approximately one-half hour.   For high permeability membranes the reduction was not as marked and although not determined precisely time lags of about two to three hours duration were still observed.   Second, the equilibrium osmotic pressure was increased over that recorded in Table III, as shown in Table IV.   This was not true of the values for grade 360, probably owing to

TABLE IV

DATA ILLUSTRATING THE "WASHING-UP" EFFECT WITH CARTER-RECORD MEMBRANES

Gelva	Conc., gm./100 cc.	Filling	π, gm./cm.²	π/C	Membrane
45	0.934	1	—	(2.26)	Carter–Record
		2 }	3.74	4.01	Low permeability
		3 }			
	1.38₅	1		(3.24)	No polymer was detected
		2 }	6.74	4.85	diffusing to solvent side
		3 }			
	1.67	1	—	(4.85)	
		2 }	9.23	5.48	
		3 }			
	2.54	1	—	(5.66)	
		2 }	18.20	7.16	
		3 }			
	0.0	—	—	(2.14)	
150	2.98	3	22.20	7.45	Membrane C and R fully swollen.
	2.45	3	14.70	6.00	Not completely semiper-
					meable to this grade.
	2.01	3	10.40	5.18	
	1.64	2	7.46	4.55	
	0.0	—	—	(1.08)	
360	1.19	1	—		
		2 }	3.36	2.82	Same as for 45 above.
		3 }			
	1.65	1		(3.31)	
		2 }	6.12	3.70	
		3 }			
	2.41	1		(4.62)	
		2 }	12.12	5.04	
		3 }			
	0.0			(0.62)	

the fact that in determining them the solution side was not washed free of polymer before being filled with a new solution, and probably also because the effect is of lesser importance with the higher polymer grades. These observations served to explain the reproducibility of the results in Table III for identical experimental procedures, and to indicate that the reason for anomalous results and extended time lags was adsorption at the membrane surface. Finally, if the procedure of allowing adsorption to occur and then washing the cell again were followed, differentiation of the polymer grades in conformity with intrinsic viscosity values was possible.

Results Obtained with Caustic Treated Membranes

Before the reason for the behaviour of C and R membranes had been determined, membranes prepared by caustic treatment were used. With these membranes the time lags to equilibrium pressure were negligible since constant readings were obtained as soon as thermal equilibrium had been established (one-half hour). This suggests that adsorption at the membrane does not occur. This is supported by two considerations, namely, that differentiation of the polymer grades in the order suggested by viscosity is possible without repeated washings, and, second, that washing of the solution half-cell does not increase the equilibrium value of the osmotic pressure. This last is illustrated in Table VII, where values for grades 15, 150, and 1700 with two caustic membranes of different preparation are given.

Data on five polymer grades obtained with caustic treated membranes are given in Table V. These data are plotted in Fig. 2.

TABLE V

Osmotic pressure measurements on a series of gelvas with caustic treated membranes

Conc., gm./100 cc.	Conc. in solvent half-cell	Membrane	Permeability to solvent	π, gm./cm.^{2}	π/C	M_n
Gelva 1700						
0.75₅	0	2% caustic	0.3*	1.26	1.67	
1.17	0	50/50 alcohol–	0.3*	2.22	1.90	
1.42₅	0	water wash	0.3*	2.46		
1.56	0	1.5% caustic water wash	0.43*	4.52	2.90	8.5 × 10⁵
0.91	0	3% caustic water wash	0.70*	1.61	1.77	
0.00	—	—	—	—	(0.30)	

The starred values represent the permeability of the membrane to solvent, uncorrected for membrane thickness, with solvent in both half-cells; the unstarred values represent the measurements made with solution in one-half cell.

TABLE V

OSMOTIC PRESSURE MEASUREMENTS ON A SERIES OF GELVAS WITH CAUSTIC TREATED MEMBRANES
—*Concluded*

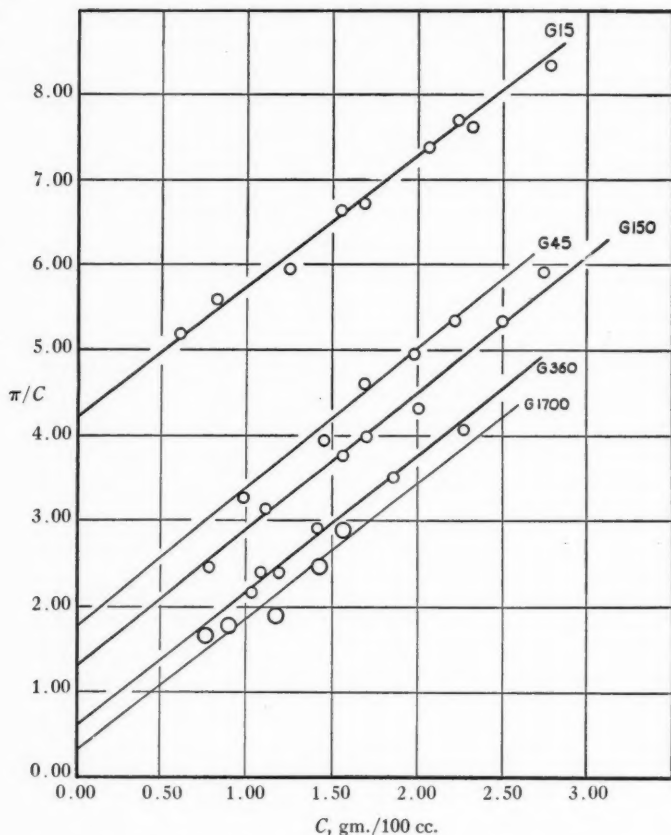| Conc., gm./100 cc.	Conc. in solvent half-cell	Membrane	Permeability to solvent	π, gm./cm.²	π/C	M_n
Gelva 360						
1.08₅	0	4% caustic water wash	0.92	2.61	2.40	
2.27	0		0.82	9.27	4.08	
1.03	0	10% caustic water wash	2.54	2.21	2.14	
1.86	0		2.42	6.54	3.51	
1.42	0		—	4.10	2.91	4.1 × 10⁵
0.00	—		—	—	(0.62)	
Gelva 150						
0.788	0	8% caustic water wash	1.24	1.92	2.44	
1.11	0		1.18	3.48	3.14	
1.70	0		—	6.80	4.00	
1.56	0	1.5% caustic water wash	0.53*	5.91	3.79	
2.01	0		—	8.65	4.31	
2.50	0		—	13.4	5.36	2.0 × 10⁵
(0.00)	—		—	—	(1.28)	
Gelva 45						
0.97₅	0	10% caustic water wash	2.68	3.18	3.26	
1.45	0		2.46	5.74	3.95	
1.68	0		2.30	7.76	4.61	
1.98	0		2.32	9.81	4.95	
2.22	0		2.10	11.88	5.35	1.47 × 10⁵
(0.00)	—		—	—	(1.74)	
Gelva 15						
2.06	0	4% caustic water wash	—	15.20}	7.39	
2.06	0		9.7	15.25}		
0.60	0		0.9	3.13	5.20	
2.78	0		0.8	23.2	8.35	
1.69	0	6% caustic water wash	1.0	11.39	6.71	
2.32	0		0.97	17.68	7.61	
1.25	0		0.96	7.45	5.96	
0.824	0		1.0	4.67	5.69	
0.0	—	—	—	—	(4.20)	6.1 × 10⁴
1.00	Slightly permeable	8% caustic water wash	1.4	4.95	4.95	
1.68			1.2	9.95	5.92	
2.37			1.06	22.60	9.55	
0.0	—	—	—	—	(4.01)	6.4 × 10⁴
2.28	Definitely permeable	10% caustic water wash	2.8	15.30	6.71	
1.77			2.6	9.66	5.46	
0.957			2.8	3.61	3.77	
2.36 }			2.5	15.65}	6.64}	
2.36 }				16.60}	7.04}	9.3 × 10⁴
0.0	—	—	—	—	(2.76)	

FIG. 2. *Osmotic pressure concentration ratio vs. concentration for a series of Gelvas.*

Comparison of Values Obtained with C and R Membranes and Caustic Treated Membranes

Typical data illustrating the difference in behaviour of the two types of membrane are given in Table VI. In Fig. 3 the values obtained for grades 45, 150, and 360 with C and R membranes by continued rinsing of the solution half-cell are compared with those obtained using caustic treated membranes.

Viscometric Results

In Table VIII are recorded data from which the intrinsic viscosity of the various polymer grades was calculated. The values of k', the constant characteristic of the solute–solvent system as suggested by Huggins (15), are given in Table IX along with the intrinsic viscosity and the number average molecular weights obtained with caustic treated membranes. It is to be

TABLE VI

SUMMARY OF OSMOTIC DATA FOR A SERIES OF GELVAS ILLUSTRATING THE EFFECT OF ADSORPTION

Gelva	Membrane	Number of** deter- minations	Time to reach equilibrium, hr.	$(\pi/C)_{c=0}$	Slope of π/C vs. C
360	Carter–Record	1	6 – 8	0.62	2.12
	Carter–Record	3	About $\frac{1}{2}$*	0.72	
	Caustic	1	About 1 – 2	0.62	1.57
150	Carter–Record	1	6 – 8	0.65	2.12
	Carter–Record	3	About $\frac{1}{2}$*	1.08	2.08
	Caustic	1	About $\frac{1}{2}$	1.28	1.55
45	Carter–Record	1	6 – 8	0.28	2.08
	Carter–Record	3	About $\frac{1}{2}$*	2.14	1.99
	Caustic	1	About $\frac{1}{2}$	1.84	1.58
15	Carter–Record	1	6 – 8	0.45	3.16
	Caustic	1	About $\frac{1}{2}$	4.20	1.54
	Caustic	3	About $\frac{1}{2}$	4.20	1.54

* These data are for low permeability Carter–Record membranes. Somewhat longer times to reach equilibrium ($\sim$ one to two hours) were found with more permeable membranes of this type, even after repeated washings.

** The numbers refer to the number of equilibrium values successively determined with each concentration.

TABLE VII

EFFECT OF REPEATED DETERMINATIONS WITH CAUSTIC MEMBRANES

Gelva	Conc., gm./100 cc.	Conc. on solvent side	Membrane	*μ to solvent	π, gm./cm.^{2}	π/C	Filling
15	1.55	0	2% caustic washed	0.30	10.2$_9$	6.64	1st
		0	with 50 : 50 alcohol	0.30	10.34	6.69	3rd
	2.23	0		0.30	17.15	7.69	1st
		0		0.30	17.1	7.68	3rd
150	1.56	0	1.5% caustic washed	0.53	8.65	4.31	1st
		0	with water	0.53	8.70	4.34	2nd
1700	1.56	0	1.5% caustic washed	0.53	4.52	2.90	1st
		0	with water	0.53	4.50	2.89	2nd

* Permeability to solvent, not corrected for membrane thickness, with solvent in both half-cells.

noted that k' does not vary appreciably throughout the series, even for a "reacetylated" sample, which is known to differ in certain respects from material which has not been hydrolysed and then reconverted to the acetate (4). Since k' depends both upon solute and solvent, it cannot be stated that a like constancy of k' would be observed in other solvents.

Relation Between Intrinsic Viscosity and Number Average Molecular Weight

The modified form of the Staudinger equation $[\eta] = KM^a$ was probably first suggested by Mark (17, p. 103) and has been repeatedly verified by Houwink (14) from data of Staudinger and Warth (20) on heterogeneous
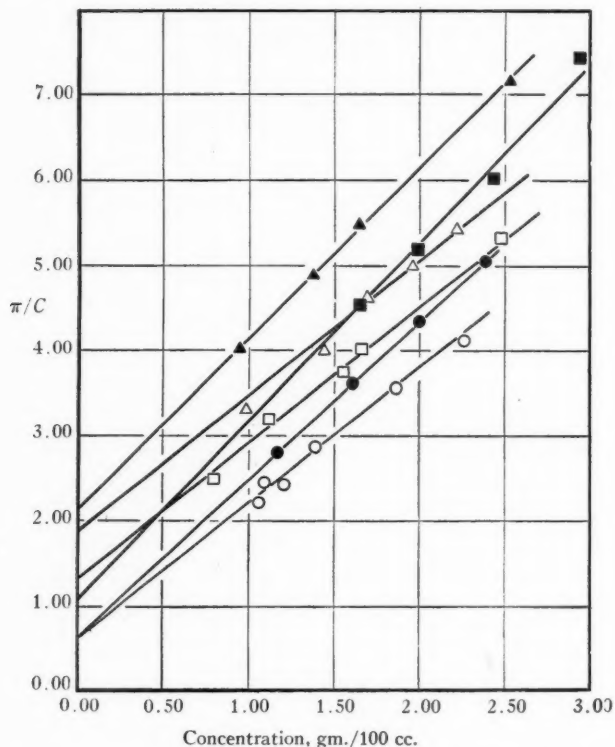

FIG. 3. *Variation in osmotic-pressure–concentration ratio with concentration for two kinds of membrane.*

	G 45	G 150	G 360
Carter–Record membrane	▲	■	●
Caustic membrane	△	□	○

samples, by Flory (9) and Mark and co-workers (1, 2) for fractionated polymers. On the assumption that each grade of this series of samples has the same degree of heterogeneity, a straight line is to be anticipated for a plot of log $[\eta]$ versus log M_n (Fig. 4). The slope of this line determines a in the above equation, and gives a value of 0.63, in excellent agreement with values obtained by Houwink, Flory, etc. The value of K will depend upon the degree of heterogeneity of the samples and therefore cannot be compared with other published values.

TABLE VIII

SUMMARY OF VISCOSITY DATA FOR A SERIES OF GELVAS

Gelva	Conc., gm./100 cc.	$\dfrac{\log \eta}{C}$	Gelva	Conc., gm./100 cc.	$\dfrac{\log \eta}{C}$
1700	0.1475	3.14	145	0.181	1.33
	0.2085	3.08		0.437	1.25
	0.2955	2.86		0.716	1.185
	0.503	2.78		0.779	1.12
	0.600	2.60		(0.0)	(1.390)
	(0.0)	(3.325)			
360	0.160	2.100	45	0.165	1.054
	0.432	1.933	Reacetylated	0.422	1.024
	0.704	1.760		0.708	0.915
	0.872	1.600		0.980	0.894
	0.0	(2.240)		(0.0)	(1.085)
150	0.133	1.74	45	0.284	0.980
	0.167	1.77		0.357	0.964
	0.290	1.71		0.414	0.965
	0.393	1.62		0.651	0.926
	0.526	1.57		0.955	0.884
	0.654	1.50		(0.0)	(1.06)
	0.0	(1.87)			
			15	0.195	0.636
				0.351	0.613
				0.492	0.640
				0.656	0.610
				0.0	0.605
					(0.650)

TABLE IX

VALUES OF INTRINSIC VISCOSITY, k', AND M_n, FOR A SERIES OF GELVAS

Gelva	$[\eta]$	k'	M_n
15	0.65	0.31	6.10×10^4
45	1.06	0.31	1.47×10^5
45			
Reacetylated	1.085	0.33	—
145	1.39	0.33	—
150	1.87	0.34	2.00×10^5
360	2.24	0.35	4.12×10^5
1700	3.32_5	0.35	8.5×10^5

In passing, it is interesting to note that the commercial samples reported on here should have approximately the same degree of heterogeneity over the wide range of average molecular weight studied.

Discussion

The existence of adsorption phenomena on cellophane membranes has been determined only for polyvinyl acetate in acetone. Some evidence exists, however, that this effect may be present in other systems. Fuoss and Mead

(10) adopted a technique of accommodating cell and membrane to polymer solution in order to avoid adsorption effects in dealing with polyvinyl chloride in methyl amyl ketone.   Moreover, these authors have remarked that in their view a membrane is not suitable unless it is swollen by the solvent
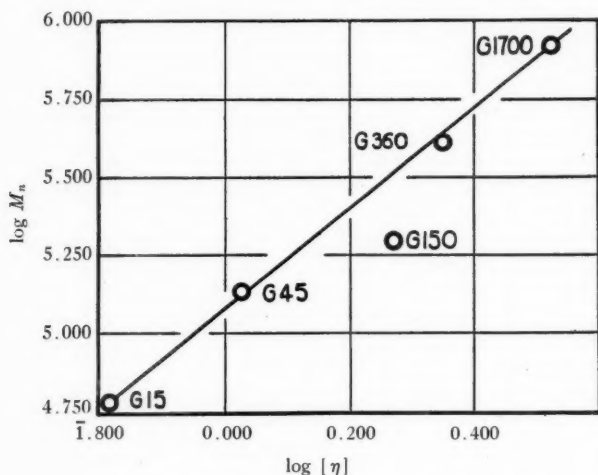

FIG. 4.   *Log M_n vs log $[\eta]$ for a series of Gelvas.*

employed, and have suggested that the reason lies in the necessity of the establishment of a phase consisting of solvent and membrane between the two half-cells.   An alternative explanation is possible in view of adsorption of solute at the membrane.   If the membrane is such that it may be readily swollen by solvent, the unsaturated forces in its surface will be preferentially satisfied by solvent, and no adsorption of solute will occur.

The most suggestive evidence that adsorption may occur with other polymer–solvent–membrane systems is the frequent reporting of extended time lags (see above).   These time lags have been reduced by stirring mechanisms (7), but never completely eliminated, a fact that has not been readily explained.   From the present investigation it is suggested that these time lags may be due to the adsorptive process at the membrane interface.

The second point of interest is the difference in osmotic pressure values determined with Carter and Record membranes and with caustic treated membranes.   As the preparation of a truly semipermeable membrane was always easier with a caustic treated type, and as both types of membrane are semipermeable within the sensitivity of the tests already described, the difference in values does not appear to be due to this factor.   Since the values with C and R membranes are always higher, this type of membrane would be expected to be more nearly perfectly semipermeable than caustic treated ones, while just the reverse was found in practice.   A striking example of

this is seen in Fig. 3, where the values for Gelva 150 were obtained with a C and R type membrane which gave a very faint cloud when tested for semi-permeability.   As anticipated, therefore, the intercept in the figure lies below that determined with a semipermeable caustic treated membrane.   At ordinary concentrations, however, the values for this membrane lie above those obtained with the caustic treated membrane.

Because of the rapidity with which equilibrium is established using caustic treated membranes, we have supposed these values to represent the true osmotic pressures.   On this assumption, and, remembering that the relation between osmotic pressure and concentration is of the form $\pi = Ac + Bc^2$ in the concentration range studied, it appears empirically that an effective concentration greater than the nominal concentration is established in the case of C and R treated membranes where repeated rinsings have been made.   On this basis both the difference in intercept and in slope of the π/c versus c plots is accounted for.   However, reference to the values obtained when the membrane is not truly semipermeable shows that the slope of the π/c versus c plot is still greater than a caustic treated membrane, although the actual concentration must be less than the nominal.

No explanation for this behaviour in terms of the known properties of solutions and rules of adsorption at interfaces is possible.   The assumption of positive adsorption of solvent at the membrane would explain the results, but as positive adsorption of solute has been indicated by experiment, this hypothesis is not tenable.   More precise measurements at lower concentrations are obviously required, and, until these have been made, it appears best to consider that a true equilibrium measurement has not been made in one or the other series of experiments.

One further observation requires emphasis.   As indicated in certain of the tables, the permeability of both types of membranes to solvent varies in a regular manner with the concentration of the solution being studied.   This was first thought to be caused by the adsorption on the membrane, but does not appear likely since both types of membrane exhibit roughly the same behaviour.   Increased viscosity of the material passing through the membrane due to the presence of small amounts of low molecular weight polymer is also a possibility, but, in view of the negative turbidity tests, this requires substantiation by further experiment.

Acknowledgment

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THE FLOW OF GASES AND VAPOURS THROUGH POROUS MEDIA[1]

By J. W. Hodgins[2], E. A. Flood[3], and J. R. Dacey[4]

Abstract

A study has been made of the flow of permanent gases (helium, hydrogen, nitrogen) and condensable vapours (diethyl ether and ethyl bromide) through a sintered glass plug. The permanent gases are transferred by a combination of Knudsen and Poiseuille flow, while the flow of condensable vapours diverges from these equations in such a fashion as to suggest surface transfer.

The flow rates of the condensable vapours begin to fall off at about 50% of the saturation pressures. Hysteresis effects are also observed in this region. It is suggested that these phenomena are caused by the condensation of small amounts of vapour in critical regions of the glass structure.

Introduction

High-boiling compounds are, in general, much more strongly adsorbed than are permanent gases, which have low boiling points. As a consequence, the adsorbed layer of a high-boiling vapour is much thicker on the adsorbent at a given temperature and pressure, and in extremely fine capillaries liquid can exist below the saturation pressure.

If a high-boiling gas or condensable vapour be forced by a pressure gradient through a medium consisting of a multitude of minute pores, it is a reasonable supposition that the adsorbed layer of vapour may cause the mobility through the pores to be different than if no adsorption occurred.

At the outset, an investigation was initiated to compare the rates of transfer of high-boiling vapours with those of permanent gases, when the vapours were forced to flow through rods of activated charcoal. The transfer rate of condensable vapours through the charcoal was found to be higher relative to the rate for permanent gases than had been expected, and divergence from Knudsen flow at low pressures was observed. However, after a series of preliminary experiments, it became apparent that knowledge of the flow characteristics through a low activity medium was desirable. Therefore, the diffusion of vapours and permanent gases through plugs of sintered glass was investigated, and this paper is a description of those experiments.

Experimental

(A) Apparatus

1. *Sintered Glass Plugs*

Pyrex glass (S.G. 2.23) was ground in an agate mortar to −100 Tyler mesh, and then ball-milled with flint stones for 12 hr. After treatment with

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hot nitric acid and thorough washing with water, the material was dried. The size spectrum of the Pyrex particles, determined microscopically, was as follows:

Particle diameter, microns	60–51	50–41	40–31	30–21	20–11	10–1.7
Number of particles in class	1	4	4	14	21	54

The average particle diameter was 12.3 μ. These particles were irregularly shaped, and for this reason each measurement was taken in the same direction, on the theory that if a sufficient number of particles were counted, the average particle diameter obtained would be correct. Most of the particles were roughly spherical—that is, no one dimension was greatly in excess of any other.

The glass powder was poured into a circular graphite mould and sintered at 650°C. into a rod 22.1 mm. long and 8.6 mm. in diameter. The plug was then sealed into a glass tube having a female 14/35 standard taper on one end. The heat required to seal the plug into the glass tube fused the periphery of the sintered glass, and thus reduced the diameter of the porous glass to 6.5 mm. It is this lesser diameter that is used in subsequent calculations. When mounted in the holder (illustrated as M in Fig. 1) the female portion of the standard taper was held against the male section with a steel spring. During the experiments, the tube containing the sintered glass plug was kept immersed in a water thermostat held at the desired temperature $\pm$ 0.1°C.

2. *Measurement of Flow Rates*

Fig. 1 illustrates the apparatus in which the flow rates of gases through the glass plug were measured. Its operation is as follows:

The gas under investigation is introduced into bulb A and burette K at pressure P_A and into bulb B at pressure P_B. The gas can be admitted either through the manifold above the bulbs, or through the ground glass joints on the sides. Bulbs A and B were insulated against sudden changes of temperature with a coating of asbestos–magnesia mixture.

The platinum contacts sealed through the wall of the manometer, L, are spaced 25 mm. apart. In each run P_A is chosen of such value that the mercury in the low arm of the manometer just touches a platinum contact. Each contact on the manometer, L, is wired to a separate terminal on the selector switch, C, with the contact on the bottom of the manometer forming a common terminal for all the circuits. When the desired pressures P_A and P_B have been set manually, the selector switch is adjusted to the contact number corresponding to pressure P_A. A potential exists between the platinum contact at the mercury meniscus and the one at the base of the manometer, such that when the circuit is closed, a current of 7 μamp. flows into the amplifier relay, D. When the pressure of the gas in bulb A and burette K falls below the desired value, the mercury in the low arm of the manometer closes the electrical circuit. The small current passing through the mercury
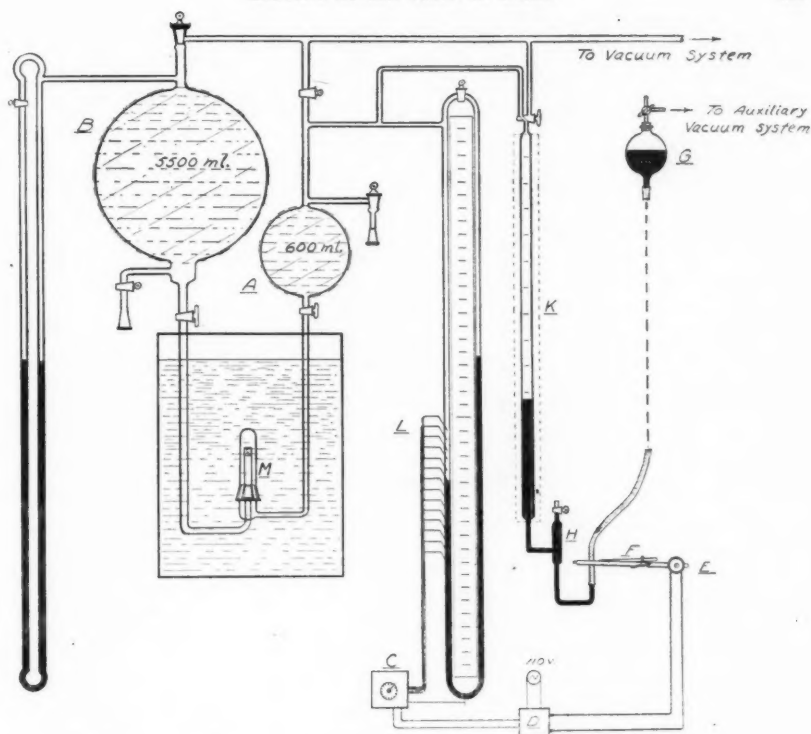
FIG. 1. *Apparatus for measuring flow of gases through porous glass plug.*

column is amplified and relayed in D, causing 5 amp. to flow through the solenoid, E. The solenoid then pulls open a pinchclamp, F, against the action of a spring, allowing mercury to flow from the reservoir, G, into the gas burette, K, thus restoring the pressure.

This manostatic control holds the pressure P_A constant to ± 0.2 mm. P_B is maintained manually; this is not difficult because of the large volume of bulb B. Exact pressures were read by means of a Gaertner cathetometer. By timing the rise of mercury in the burette, the rate of passage of gas through the sintered glass plug is obtained.

For all the experiments involving ethyl ether and ethyl bromide, the ground glass surfaces in the system were lubricated with a lubricant resistant to organic solvents (7).

3. *Apparatus for Ascertaining Interstitial Volume*

It was desirable to know what percentage of the spatial volume of the glass lattice is composed of micro pores between the glass particles. By micro pores, holes having a diameter of the order of 3×10^{-4} cm. and smaller are indicated. Pure mercury at 25°C. and 1 atm. pressure will not enter voids of microscopic

or colloidal dimensions (5, p. 80). The over-all volume of the glass lattice was therefore obtained by means of the apparatus illustrated in Fig. 2.
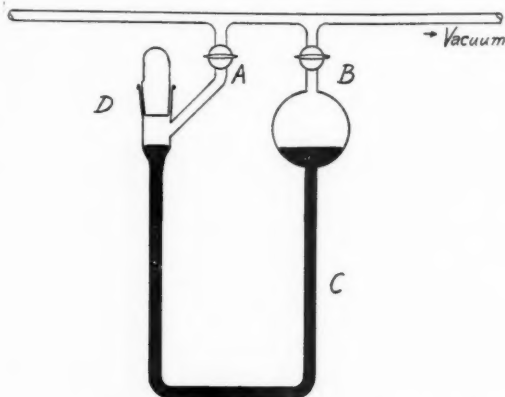

FIG. 2.   *Apparatus for the determination of apparent density by mercury displacement.*

The operation of the apparatus is as follows. The illustration shows the level of the mercury in the apparatus with 1 atm. pressure in each tube. With taps A and B open, the space above the mercury is thoroughly evacuated. Tap A is closed, and air at 1 atm. pressure admitted through tap B; this forces the mercury to completely fill volume D. When D is completely filled, the mercury in the microburette C (5 ml. burette, graduated to 0.02 ml.) gives a reading near the bottom of the scale. Atmospheric pressure is then restored at A and B and the sample is introduced into volume D by way of the cap. The mercury is then forced under 1 atm. pressure to fill volume D as before, and a second reading taken on the burette tube. The difference between readings is the volume of the glass plus the micro pore volume. From the weight of the plug and the accurately known specific gravity of Pyrex, the actual volume occupied by the glass in the plug is readily obtained and the micro pore volume calculated.

4. *Measurement of the Ether Adsorption Isotherm of the Glass Plug*

The isotherm measurements were made on a McBain–Bakr (6) balance, a long and sensitive quartz fibre being employed and the extension of the spiral being observed through a 40-power microscope with a calibrated eyepiece scale. The spiral had a sensitivity of 0.54 mm. per mgm. load, and the microscope magnified the movement to 0.046 mgm. per scale division.

5. *The Gases*

The gases and vapours used in these experiments are listed below, together with their viscosities at 35°C., their molecular weights, and their source.

The three permanent gases were admitted to the system through liquid air traps to remove any condensable impurities. Except for this precaution,

Gas or vapour	Viscosity at 35°C., micropoises	Molecular wt.	Source
Helium (4)	202.5	4.003	U.S. Govt. Cylinder
Hydrogen (12)	90.3	2.016	Ohio Cylinder Gas Co.
Nitrogen (12)	181.5	28.016	Dom. Oxygen Company
Diethyl ether (10, 11)	77.4	74.12	Merck Reagent Chemical (distilled from sodium)
Ethyl bromide (9, 11)	180.0	108.98	Baker and Adamson, Reagent Chemical

the gases were used as received in the laboratory, without any attempt at additional purification. The nitrogen was analysed for oxygen prior to its use; the oxygen content was 0.2%. Since the hydrogen was made electrolytically, it was presumed to be quite pure. The helium, however, probably contained a trace of impurity, which changed its viscosity slightly, for the data obtained in the helium experiments were not quite consistent with those of the other two gases. This particular selection of materials was made so as to provide a range of molecular weights, viscosities, and boiling points.

(B) Experimental Results

The flow rate measurements were made on the apparatus illustrated in Fig. 1, using a 50 mm. pressure gradient across the plug, at mean pressures varying from 25 to 675 mm. in 50 mm. steps. All the data listed were obtained by measuring the gas flow over a 30-min. period. This fact is important when regarding the hysteresis effects observed with the condensable vapours. Unless otherwise stated, the temperature was 35°C. ± 0.1°C. during all the runs.

The numerical results are listed in Table I and are represented graphically in Figs. 3 and 4.

The lines in Fig. 3 have all been calculated to the best fit of the data by the method of least squares.

It is now proposed to apply conventional flow equations to the experimental data obtained.

The two common equations expressing the mechanism of gaseous transfer in cylindrical tubes are Poiseuille's equation for streamline flow, and Knudsen's equation for molecular streaming.

Poiseuille's equation

$$\frac{dn}{dt} = \frac{r^4 \pi \bar{P}(P_A - P_B)}{8l\eta RT}$$

describes the flow occurring in a tube whose diameter is large compared to the mean free path of the gas molecules. It is therefore the flow equation describing gas transfer at high pressures. In its simplest form, it may be written

$$\frac{dn}{dt} = \frac{a\bar{P}(P_A - P_B)}{\eta},$$

TABLE I

FLOW RATE OF GASES THROUGH SINTERED GLASS PLUG

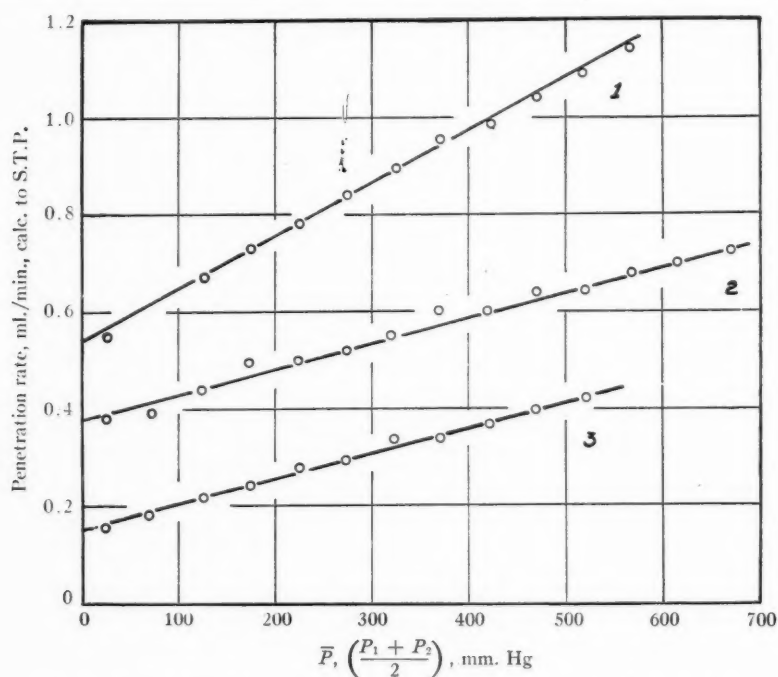| $\overline{P}$, or $\dfrac{P_A+P_B}{2}$, mm.	Volume passing per minute, in ml. calculated to S.T.P.				
	Ethyl ether	Ethyl bromide	Helium	Hydrogen	Nitrogen
26.0	0.08	0.091	0.380	0.550	0.157
76.0	0.154	0.141	0.392	0.60	0.183
125.5	0.244	0.207	0.44	0.67	0.22
174.0	0.341	0.245	0.495	0.73	0.24
223.0	0.47		0.50	0.78	0.28
273.1	0.490	0.376	0.52	0.85	
322.0		0.381	0.55	0.895	0.34
370.7	0.64	0.391	0.60	0.955	0.34
421.3	0.66		0.60	0.985	0.37
468.8			0.64	1.04	0.41
518.0			0.64	1.09	0.42
566.9			0.68	1.14	
615.4			0.71	1.16	
669.8			0.72		

FIG. 3. *Rate of flow of permanent gases through porous glass plug. Curve 1—hydrogen; Curve 2—helium; Curve 3—nitrogen.*

showing the dependence of flow rate directly on the mean pressure and inversely on the viscosity.

Knudsen's equation expresses the condition of gas transfer when the mean free path is large compared with the tube diameter, and is thus the equation holding for low pressures.
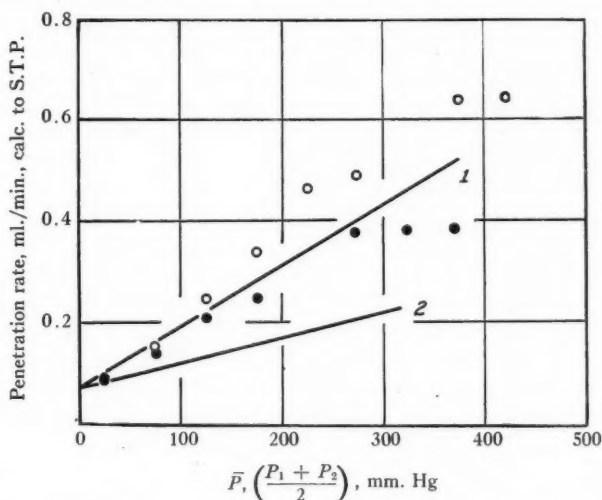

FIG. 4. *Rate of flow of vapours through porous glass plug. ○—Experimental values for diethyl ether. ●—Experimental values for ethyl bromide. Curve 1—Diethyl ether as predicted by Knudsen–Poiseuille flow. Curve 2—Ethyl bromide as predicted by Knudsen–Poiseuille flow.*

The equation is:

$$\frac{dn}{dt} = \frac{4}{3}\frac{r^3\sqrt{2\pi}(P_A - P_B)}{l\sqrt{MRT}},$$

and can be simplified to

$$\frac{dn}{dt} = \frac{B(P_A - P_B)}{\sqrt{M}}.$$

The flow-rate is thus independent of the mean pressure and proportional to $\frac{1}{\sqrt{M}}$.

Bearing these two equations in mind, it is apparent that somewhere along the pressure scale, Knudsen flow will give way to Poiseuille flow, and, at the point of change-over, the flow rate will cease to be proportional to $\frac{1}{\sqrt{M}}$, and will become proportional to $\frac{1}{\eta}$. H. Adzumi (1, 2), in his experiments on the diffusion of permanent gases through earthenware plates, found that the above two types of flow did overlap, and he combined the two equations into one, taking into account an added factor, γ, the coefficient of slip.

His modification of the flow equations is

$$\frac{dn}{dt} = \frac{\pi}{8\eta RT} \cdot \frac{\bar{P}N\bar{r}^4}{l}(P_A - P_B) + \gamma\frac{4}{3} \cdot \frac{\sqrt{2\pi}}{\sqrt{MRT}} \cdot \frac{N\bar{r}^3(P_A - P_B)}{l}.$$

This may be simplified to

$$G = \frac{\pi}{8\eta RT} \cdot \frac{\bar{P}N\bar{r}^4}{l} + \gamma\frac{4}{3}\frac{\sqrt{2\pi}}{\sqrt{MRT}} \cdot \frac{N\bar{r}^3}{l},$$

where G = flow rate per unit time per unit pressure gradient,

N = number of pores in the plug in question,

$\bar{P}$ = mean pressure = $\dfrac{P_A + P_B}{2}$,

$\bar{r}$ = effective average pore radius,

l =   "   "   " length,

η = gaseous viscosity,

γ = coefficient of slip, and, where there is no specular reflection of
    .   gas molecules from the pore walls, may be evaluated as 1.0.
         For the pressure range in question, γ was taken as 0.9.

M = molecular weight of gas.

The above equation is the equation of a straight line representing the variation of the flow rate through the glass plug as a function of the mean pressure. The slope of the G vs. $\bar{P}$ curve gives the value of $\dfrac{\pi}{8\eta RT} \cdot \dfrac{N\bar{r}^4}{l}$, and the intercept on the G-axis evaluates $\dfrac{4}{3} \cdot \dfrac{\sqrt{2\pi}}{\sqrt{MRT}} \cdot \dfrac{N\bar{r}^3}{l}$. Dividing the former by the latter gives the value of $\bar{r}$.

For the permanent gases straight lines were obtained when the rate of flow was plotted against the mean pressure as seen from Fig. 3. The values of $\bar{r}$ from these curves are $1.34\,\mu$, $1.16\,\mu$, and $1.16\,\mu$ for helium, hydrogen, and nitrogen respectively. Using an average value of $1.2\,\mu$ the number of pores was calculated to be 3×10^5 in the plug in question.

With the condensable vapours (see Fig. 4) not only does a falling-off of rate occur at about 50% saturation pressure, but the data at lower pressures do not fit a straight line. However, if the line of best fit is drawn through these points, values of $\bar{r}$ calculated are $3.6\,\mu$ and $3.2\,\mu$ for ethyl ether and ethyl bromide, while the values of N were 1×10^4 and 2.5×10^4. It is therefore concluded that the behaviour of the condensable vapours is not in accordance with the Poiseuille–Knudsen equation. The straight lines appearing in Fig. 4 represent the behaviour of the condensable vapours, assuming that their behaviour corresponded with that of the three permanent gases. It is apparent that, at the very low pressures, the experimental data conform with this assumption. As the pressure increases, the flow rates of the vapours are higher than those predicted by Poiseuille–Knudsen flow up to the point where the falling-off occurs.

Now, since the glass plug was made from glass particles of mean diameter 12 μ, it would be of interest to see whether the pore size as obtained from the flow equations is of the same order of magnitude as the average pore size calculated from the geometry of the packing in the plug. To make this calculation, an estimate was necessary of the type of packing that existed in the plug after sintering. Since the percentage of voids in the lattice is some indication of the arrangement of the particles, a mercury density measurement was made on a portion of the plug, using the apparatus described above. The lattice was found to be composed of 24.4% voids, which corresponds fairly well with the figure for closest packing of spheres (25.95%)(3). Assuming, then, that the arrangement of the particles in the plug approximates the rhombohedral packing of spheres, the mean pore radius was calculated by the method of W. O. Smith (8). The figure calculated for the mean pore radius by this method was 1.7 μ, in good agreement with the flow radius of 1.2 μ for the permanent gases. Assuming the same arrangement, the number of pores per square centimetre for 12 μ spheres is 8×10^5 as compared to 9.9×10^5 calculated from the flow equation.

As can be seen from Fig. 4, for both ethyl ether and ethyl bromide, a falling-off of flow rate was observed, considerably below the saturation pressure for each vapour. At 35°C. the falling-off occurs at about 275 mm. for ethyl bromide and about 375 mm. for ether vapour. Further investigations brought out the following observations:

(*a*) The penetration rate of a condensable vapour through the porous glass plug at a pressure exceeding 60% of the saturation pressure decreased to an equilibrium value after the plug had been exposed to the vapour for a sufficiently long time. The rate reached at equilibrium was always of the order of 90% of the rate obtained by extrapolation of the first part of the G vs P curve.

(*b*) The values for G, obtained from 30-min. runs with ether vapour at 25°C., were true equilibrium values only up to about 160 mm. pressure, and the equilibrium values in every case above 160 mm. were lower than those obtained from a 30-min. run.

(*c*) After the glass plug had been equilibrated for 18 hr. to ether vapour at 25°C. and 446 mm., the pressure was lowered and a diffusion rate measurement was carried out immediately at a mean pressure of 126 mm. The rate obtained on a 30-min. run under these conditions was considerably lower than that observed when measurements were made directly, without previous equilibration. However, the rate continued to increase throughout the 30-min. period. On letting the plug stand for five hours at 126 mm., a new diffusion rate measurement showed a return to the original value. This experiment demonstrated the hysteresis.

The McBain–Bakr balance was used to determine whether any measurable amount of ether was adsorbed at the pressures at which the flow experiments were carried out. The measurements were made at 25° C. using two sections cut from the glass plug, weighing 0.4428 and 0.3546 gm. In no case was any

adsorption detected below 92% saturation pressure. With a glass fragment weighing 0.4428 gm., 0.07 mgm. was adsorbed after one hour at an ether pressure of 493 mm.   Below this pressure, in the region where the flow experiments were made, the ether adsorbed could not be detected with the apparatus used.
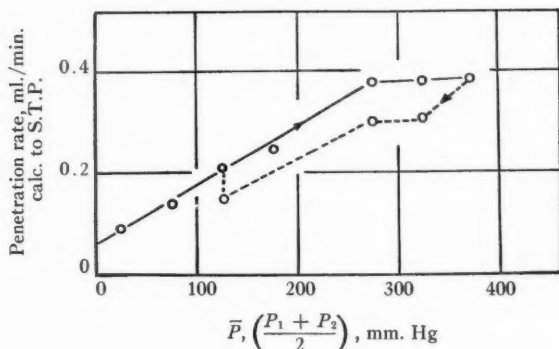

FIG. 5. *Hysteresis effect as observed for ethyl bromide flow through sintered glass plug.*

Discussion

The permanent gases, when flowing through the sintered glass plug, are transferred by a combination of Knudsen and Poiseuille flow, consistent with gaseous flow through fine capillaries.   The average effective pore radius of $1.2\,\mu$ determined for the permanent gases agrees well with the value of the average radius of the interstices between closest packed $12\,\mu$ spheres.

Two anomalies are exhibited in the transfer of condensable vapours through the sintered glass plug.   First, the flow rate begins to fall off rather suddenly at a relative pressure of about 50% of the saturation pressure, hysteresis being also observed in this region.   Second, below this pressure the rate of transfer is higher than that predicted by Poiseuille–Knudsen flow, the divergence increasing as the pressure increases.

The latter of these phenomena suggests that some other method of transfer exists in addition to ordinary gaseous flow.   This may be the flow along the surfaces of an adsorbed layer, which no doubt exists on the glass although the sensitivity of the adsorption apparatus used could detect no adsorption at the lower pressures.

The falling-off of flow rate of the vapours at a fraction of the saturation pressure, and particularly the hysteresis associated with it, suggests that this phenomena is caused by physical adsorption or condensation.   The medium is composed of packed granules and the spaces between are a series of fairly large voids interconnected by narrow necks and not a bundle of parallel capillaries as assumed by Adzumi.   If we assume that at the points of constriction where the actual radius is very much less than $1.2\,\mu$, some capillary

condensation occurs, blocking a sufficient number of paths to reduce the flow rate by the amount observed, we have a mechanism explaining the phenomena. The quantity of material necessary for this effect could be very small and escape detection in the adsorption apparatus. This view is strongly supported by the hysteresis effects, which are difficult to explain in any other way.

The following conclusions are drawn from the investigation:

(i) For the flow of permanent gases, a sintered glass plug may be regarded as a bundle of parallel capillaries, and the conventional treatment gives satisfactory results.

(ii) A porous medium, even as inert as glass, cannot be correctly regarded as a system of parallel cylinders when a mathematical treatment is employed to describe the transfer of condensable vapours. The evidence of surface flow and the blocking-off and hysteresis effects invalidate the simple picture in this case.

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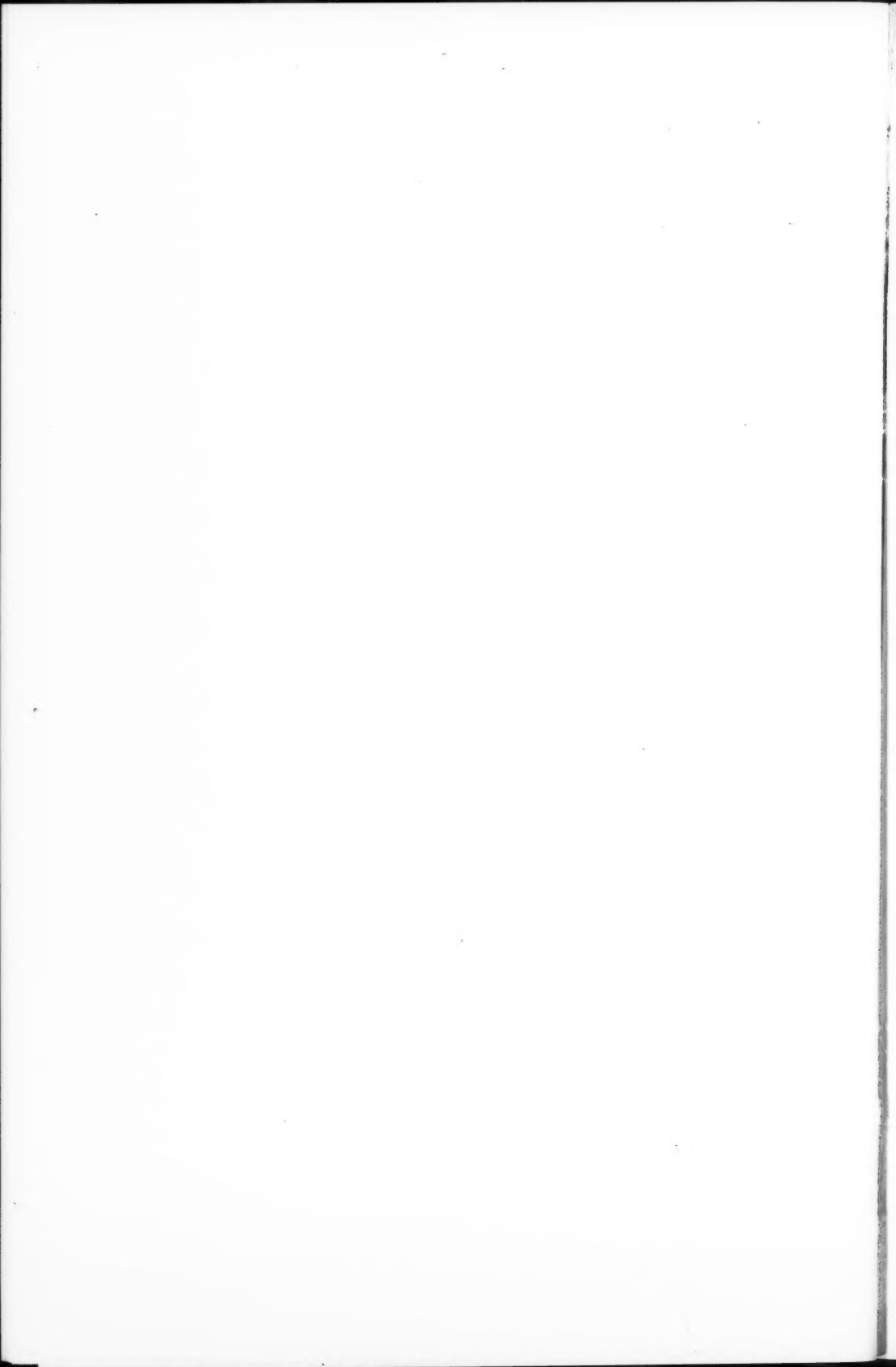
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